FOREWORD

This two-volume report contains the results of a detailed study of international scope by Soletanche and Rodio, Inc. to determine the feasibility of developing cheaper chemical grouts from non-petroleum materials. The report was first written in French and then in English. The reader may note a few unusual expressions illustrating one difficulty in translation. The report contains a wealth of information about all types of chemical grouts applicable to soils and recommends laboratory test procedures for evaluating chemical grout.

Sufficient copies of the report are being distributed to provide two copies to each regional office, one copy to each division office, and two copies to each State highway agency. Direct distribution is being made to the division offices.

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This report does not constitute a standard, specification, or regulation.

Charles F. Scheffey
Director, Office of Research
Federal Highway Administration
The essence of this research is the search for more economical grouts not directly dependent on petroleum. The study has required an extensive investigation of 75 years of knowledge on chemical grouts in order to clear out the present diaspora of products. From this a general classification of chemical grouts has been proposed based on the nature of the major component. The grout materials were evaluated on the basis for several factors: injectability, permeability, setting time, strength of pure grout, strength of grouted soil, durability, toxicity. Grout families of substantial interest have been tested following these standards; further, a selected number of grouts have been tested for possible improvement. These tests indicate that lignochrome gels and furan resin derivatives are particularly promising.

A companion report, Volume II (FHWA-RD-77-51), is entitled "Engineering Evaluation of Available Materials."
This is Volume I of a two-volume report entitled "Chemical Grouts for Soils". Volume I (FHWA-RD-77-50), entitled, "Available Materials", contains a comprehensive study of written data, available in the international community, from the beginning of grouting around the turn of the century to current times. A classification of grouts is proposed based on the main components. References to bibliography made in both volumes will relate to Chapter IX of this volume, where bibliographical references are classified chronologically.

Volume II (FHWA-RD-77-51), entitled "Engineering Evaluation of Available Materials", discusses the various testing procedures available for defining the engineering characteristics of a chemical grout, proposing a single procedure for standardization for each of the seven selected engineering criteria.

The most promising of available grout materials were selected for further study, based on non-dependence on petroleum products. Finally, lines of research into the improvement of these materials are suggested and partially implemented.

This report is the result of a team effort involving the Soletanche Group grouting experts and laboratory control organisms, public authorities, and the chemical industry.

Because of traditional secretiveness of the chemical industry, no accurate economical data related to energy requirements for manufacturing have been available, although technical information has always been provided graciously.

No special distinction is made in relation to cut-and-cover and soft ground tunneling situations except that considerations of validity and economy are always taken for large projects where grouting is used as a construction method and not an expedient solution to a short-term problem.
ACKNOWLEDGMENTS

The list would be too long to cite all individuals or organizations whose contribution has enriched the substance of this report, and the authors take this opportunity to thank them jointly.

Special acknowledgment must be made of the judicious and friendly guidance and criticism of J. R. Sallberg, Contract Manager for the Federal Highway Administration.
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GLOSSARY OF TERMS

Activator. Catalyst, hardener, reagent. The chemical solution which causes a mixture to gel or set when mixed with the base solution.

Alluvium. Clay, silt, sand, gravel, or other rock materials transported by flowing water and deposited in comparatively recent geologic time as sorted or semisorted sediments, in riverbeds, estuaries and flood plains, on lake shores and in fans at the base of mounting slopes.

Agglomerating Power. See Cohesion.

Arrhenius Rate Law. The speed of a chemical reaction is affected by changes in temperature.

\[ k = \frac{Ae^{-E_A/RT}}{RT} \]

A, \(E_A\) are constants characteristic of reacting substances
R is thermodynamic gas constant
T is temperature in °Kelvin

Bar. Measure of compressive strength. \(1 \text{ kg/cm}^2 = 0.981 \text{ bar} \)

\(1 \text{ bar} = 14.56 \text{ psi} = 100,000 \text{ Pascals (}10^5 \text{ Pa}).\)

Baume Degrees. Indication of the density of a liquid (°B), measured with a Baume hydrometer. (36.6 °B = 1.340 density).

\[ °B = 144.38 \frac{(\text{density} - 1)}{\text{density}} \]

Bentonite. A montmorillonite-type clay formed by the alteration of volcanic ash which swells in the presence of water.

Bingham Fluid. A true solution which, in addition to viscosity, tends to exhibit a certain rigidity so that, up to a certain gradient, it will behave as a solid.

Catalyst. See Activator.

Coefficient of Permeability. The rate of discharge of water under laminar flow conditions through a unit cross-sectional area of a porous medium under a unit hydraulic gradient and standard temperature conditions.
Cohesion. Agglomerating power. The capacity of sticking or adhering together. The cohesion of soil or rock is that part of its shear strength which does not depend on inter-particle friction.

Consolidate, Consolidation, Grouting or Solidify. Terms applied to the binding together of soil particles into a mass of soil, such as occurs in permeation grouting.

Cut-and-Cover Tunneling. A process of installing a structure below ground by excavating an area of sufficient width, constructing the permanent structure at the bottom of the excavation, and then restoring the ground surface over the structure.

Darcy's Equation. The formula developed by Darcy to determine permeability:

\[ K = \frac{Q}{t} \times \frac{1}{S} \times \frac{e}{p} \]

- \( K \) is the permeability coefficient
- \( t \) is time
- \( Q \) is quantity of water
- \( P \) is pressure
- \( e \) is thickness of sample
- \( S \) is section of sample

Darcy's Law. Formula developed by Darcy to determine speed of percolation in permeability testing:

\[ V = ki \]

- \( V \) is speed of percolation, cm/sec
- \( k \) is permeability coefficient (Darcy), cm/sec
- \( i \) is gradient applied to sample, cm/cm
  (function of pressure and sample thickness)

Deformability. A measure of the elasticity or stress deformation characteristics of the grout in the interstitial spaces as the earth mass moves.

Density. Mass per unit volume of a substance in g/cm\(^3\).

Diaphragm Wall. The construction of a vertical, continuous concrete wall, cast in situ or made of precast concrete panels, in a narrow trench filled with bentonite slurry to form a structural retaining wall.

Groundwater Table (Free Water Elevation). Elevations at which the pressure in the water is zero with respect to the atmospheric pressure.
Grout. A suspended cement or clay slurry or a chemical solution that can be poured or forced into the openings between soil or rock particles to solidify or to change the physical characteristics of the material.

Groutability. The ability of soil to allow grout to be forced into the interstitial spaces between the particles. As applied to grout material, its ability to be forced into the interstitial spaces between soil particles.

Hydrostatic Head. The pressure in the pore water under static conditions; the product of the unit weight of the liquid and the difference in elevation between the given point and the free water elevation.

Injectability. See Groutability.

Injection. Grouting. The process of forcing a grout into the soil to be treated, using pressure.

Joosten Process. The earliest of the chemical grouting processes, originating in 1925. In this process, a sodium silicate solution is pumped into the soil as a grout pipe is advanced downward. The pipe is then flushed with water, and calcium chloride is pumped in as the pipe is retracted. A precipitate forms upon contact between the two solutions.

Karst. An irregular limestone region with sinks, underground streams, and caverns.

Newtonian Fluid. A true solution which tends to exhibit constant viscosity at all rates of shear.

Permeability. See Coefficient of Permeability.

Permeation Grouting. Replacing the water or air in the voids of the soil mass with a grout fluid at a low injection pressure to prevent creation of a fracture, permitting the grout to set at a given time to bind the soil particles into a soil mass.

Porosity. The ratio of the volume of the voids or pores to the total volume of the soil.

Reagent. See Activator.

Resin. A synthetic addition or condensation polymerization substance or natural substance of high molecular weight, which under heat, pressure, or chemical treatment becomes a solid.
Setting Time. The time needed for a chemical grout to solidify.

Slurry. Suspension of cement or clays in water, or a mixture of both.

Slurry Trench. A relatively narrow trench which is usually dug with a clamshell while the excavated portion is kept filled with a bentonite slurry to stabilize the walls of the trench.

Specific Gravity. Ratio of the mass of a body to the mass of an equal volume of water at a specified temperature.

Star Wheel. The vane used with a Vane Test, to determine shear strength; when viewed from above, the vane is star shaped.

Syneresis. When freshly prepared sodium silicate gel is placed in a closed glass container, a significant amount of water can be observed being extruded by the gel. This is the phenomenon of syneresis, which is peculiar to silica gels.

Toxic. Poisonous or harmful.

True Solution. One in which the components are 100% soluble in the base solvent.

Tube a Manchette. A plastic tube or pipe of approximately 1-1/2" inside diameter, perforated with rings of 4 small holes at intervals of about 12 inches. Each ring of perforations is enclosed by a short rubber sleeve fitting tightly around the pipe so as to act as a one-way valve when used with an inner pipe containing packing elements which isolate a hole for injection of grout.

Tyndall Effect. Visual scattering of light along the path of a light beam as it passed through a system containing discontinuities, such as surfaces of colloidal particles in a colloidal dispersion.

Unconfined Compressive Strength. The load per unit area at which an unconfined prismatic or cylindrical specimen of material will fail in a simple compression test.

Vane Shear Test. Device for measuring shear strength. A 4-bladed vane is attached to the bottom of a vertical rod. The assembly is lowered into the material to be tested and rotated. The torque required to turn the vane is measured and shear strength is computed using the torque measurement and the dimensions of the vane.
Viscosity. The ratio of the tangential frictional force per unit area to the velocity gradient perpendicular to the direction of flow of a liquid.
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CHAPTER I
CLASSIFICATION AND EVALUATION

1. Introduction

This survey and study of chemical grouts has as its goal the listing of all available chemical grouting materials in an attempt to find effective chemical grouts which do not use petroleum products.

Most available chemical grouts use some kind of petroleum products or derivatives either in the grout or in the grout reagent. Because of the very real possibility that supplies of petroleum may be reduced substantially in the future, it has become necessary to develop alternate chemical compounds to replace petrochemicals.

In the course of research into the available literature, many grout formulas were discovered, some of which have been used extensively, some of which may never have been used. Of the grouts which have been used and documented, all were classified in groups, according to the major component. Each grout category was then studied and rated according to seven quality/price criteria.

The final chapter of this volume is a complete listing of bibliographical references, including many patents. References are given in chronological order.

Volume II deals with engineering qualities of grouts, developing seven criteria for evaluation of these qualities and discussing the various testing procedures available. The most appropriate test method for each criterion is proposed for standardization in order to make test results comparable from one laboratory to another.

The most dependable grouts from the general classification are evaluated in detail, using the engineering criteria developed. The most promising of these materials, in terms of reliability and non-dependence on petroleum, are again studied pinpointing the advantages and disadvantages of each. In a final selection process, two non-petroleum materials are selected for research into possibly eliminating or reducing the major drawbacks to their use as chemical grouts.

2. Chronological Development of Chemical Grouts

Grouting was initiated during the first part of the nineteenth century; in 1802 Charles BERIGNY injected clay grouts and lime hydraulically. In 1856 W. R. KINIPPLE
introduced this method into England. In 1876 Thomas HAWSLEY used Portland cement grout for the first time to consolidate fissured rocks. This technique was improved between 1880 and 1905 by engineers such as REUMAUX, PORTIER, SACLIER and FRANCOIS.

Techniques based on cement grout were evidently not feasible for the treatment of sands or other fine formations which require non-granular grouts with low viscosity. This gap was filled by the JOOSTEN-JEZIORSKY technique, based on sodium silicate, for which the first patent was issued in 1886. For 65 years, until approximately 1955, chemical grouts were based on sodium silicate to such an extent that, during all this period, any mixture with a silicate base was called "chemical grout".

The JOOSTEN-JEZIORSKY technique (concentrated sodium silicate injected through a bore-hole, and a solution of calcium chloride injected under high pressure through a neighboring hole), was modified through the years. In 1911, the FRANCOIS procedure (calcium chloride replaced by aluminium sulfate) and the GUTTMANN technique (addition of sodium carbonate) were developed. These techniques permit adequate consolidation of injected sands; they have been used extensively, especially in anglo-saxon countries. Unfortunately, they require two phases and have all the inconveniences inherent in such a system: twice as many bore-holes are needed than for a one-shot technique, the pressure for grouting must be high, and the in situ mixture of silicate and its reagent is not always perfectly accomplished.

A series of single-phase procedures appeared during the beginning of this century. The pioneers in this field were LEMAIRE and DUMONT (1909), FRANCOIS, GAYARD and RODIO. The common denominator in all of these techniques is sodium silicate, used in very dilute solution. These methods are strictly for waterproofing. In practice, it seemed that, if the sodium silicate were sufficiently dilute, most acids or polyvalent salts would act to retard gelification sufficiently to permit a one-phase grouting operation. Since then, scores of reagents for waterproofing gels have been proposed for use. Many of them are now of historical interest only. More than 75% of waterproof grouting uses gels calling for sodium silicate reagents such as sodium bicarbonate, sodium aluminate and alumina sulphate.

Aside from sodium silicate-based gels, nothing promising appeared until 1955, when some experiments were made on lignochrome gels (lignosulfonate solution added
to an alkaline dichromate), as well as experiments on bitumen (warm or emulsified). Grout classification in 1955 was rather simple, since grouts would fall into one of two categories, both derived from sodium silicate:

1. Concentrated biphase systems, limited to fine soil consolidation.
2. Diluted monophase systems, limited to ground waterproofing.

Around 1955, thanks to organic chemistry, there were important developments in chemical grouts which allowed the use of grouts better adapted to different types of soils. This input from organic chemistry first affected sodium silicate. In all these systems, instantaneous setting of the silicate in the mixer could be prevented only by either working in two phases, with all the inconveniences inherent in this method, or by diluting the sodium silicate to a great extent, resulting in waterproofing the ground without consolidation.

Discoveries made between 1957 and 1959 made it possible to obtain a retarded gelification of the sodium silicate, using an organic reagent which is initially inert in relation to the silicate in the one-shot application. The first reagents found for this purpose were:

Aliphatic esters, such as ethyl acetate, methyl acetate, propyl formate. The basic principle is the saponification of the ester with gradual liberation of the silicate by neutralizing the soda. (C. CARON: "New Method for Gelification of Alkaline Silicate and Use of New Products Resulting in Waterproofing and Consolidation of Soils and Other Porous Matter." CARON F. P. 1,164,835, 1957).

Glyoxal, a dialdehyde. By internal Cannizaro reaction, it slowly releases a glycolic acid which neutralizes the sodium in the silicate and precipitates the silica. (GANDON LEHMANN, MARGHERET, TARBOUR-IEGH: "Gel Changeable into a Matter Having the Properties of a Cement and Fabrication Procedure of these Products." F. P. 1,166,581, 1958).

Acid chlorides. Gelification of the silicate is obtained by hydrolysis of an acid chloride which liberates the corresponding acid. (SCHMIDT and GEDEMK: "Waterproofing and Consolidating Products for Soils and Masonry." W. G. P. 139-14/59, 5/26/59).

At this stage, a major improvement in sodium silicate based grouts was made through macromolecular chemistry. Cold polymerization could be obtained in the ground, starting from aqueous monomers and within a precisely determined period of time.

All of the systems based on sodium silicate allow very good ground injection, both for watertightness and consolidation of sands. However, grouting can become difficult in fine sand, since all silicate-based grout has a viscosity greater than water. When high strength consolidation is desired, increased concentration of the silicate is necessary, resulting in increased viscosity. To be suitable for penetrating very fine sands, grouts with viscosity equal to that of water must be used. These grouts are obtained from liquid resins of low viscosity that polymerize at normal temperatures. In this category, the first three grouts to have been developed are:

Acrylamide: Its base product is AM-9, patented by American Cyanamide Co., and first used for grouting purposes in 1958.

Urea formaldehyde: Its polymerization in acid media has been known for a long time. It has been used as a grout since 1960, but cannot be used in limey soils without a preliminary acid washout of the ground.

Resorcinol-formaldehyde: This grout does not present the inconvenience of urea-formaldehyde grout as it can also polymerize in a basic medium (C. CARON P.P. 1,248,651.11/13/1959).

3. Bibliographical Research

For the last fifteen years, macromolecular chemistry, plus a few new principles, has led to such a mass of variations in grouts based on the same principles, that there is now a plethora of compositions and patents which often duplicate or triplicate the basic composition.
All existing products are discussed in the references listed in this report, whether the grouts are used or not. The bibliographical research resulted in a list of some 1,200 references. Close examination has shown that some of them have little to do with the subject at hand, and these have been eliminated, leaving some blanks in the final bibliography.

Numbering of references is done with a set of four figures. The first two numbers are explained as follows:

00 for articles published prior to 1900
01, 02, .. for 1901, 1902,..
99 for suppliers' catalogues (usually undated).

These first two numbers are followed by a filing number which will permit immediate retrieval. References on pure chemistry have not been reported.

Several base articles include a partial or complete study of a number of grouts. These are given below with the reference number which they bear in the report. These base articles or books have not been further cited systematically according to each grout.


58-03 Chemical Soil Solidification in Foundation-Water Control and Tunnel Work. Riedel, C.M. 6th Annual Conf. on Soils Mechanics and Foundation Engineering, Univ. of Minnesota, Minneapolis, Minn. 1958, pp. 37-44.


Finally, numerous articles concerning ground surface stabilization were consulted. While these articles do not deal specifically with injection, there is an interesting correlation between surface and subsurface stabilization, notably at the level of the products used. Below is a list of the basic articles on surface stabilization which were used in the editing of several chapters on injection.


4. Criteria for Defining a Chemical Grout

Chemical grouts are reserved for use in soils with a grain size of less than a millimeter. In addition, the particle size of the grout must be much smaller than the grain size of the soil to be grouted (LEONARD 61-16). In reality, the grain size of a good chemical grout should not be more than several microns. For the same reason, the viscosity of the grout should not exceed about 20 cP, whether for Newtonian liquids (true solutions or emulsions), or for Binghamian liquids of slight rigidity (colloidal solutions), although for special cases, a higher viscosity could be permitted. In addition, the grout must remain stable during preparation and injection. Thus, a suspension should settle only when in place in the ground. Finally, the grout, when in place, must be able to resist chemical attack and erosion caused by water in the subsoil; and, in the case of consolidation, it will have to be able to resist various stresses.

5. General Classification of Chemical Grouts

This classification of grouts is based on the nature of the principal ingredient of the grout. Much of the report elaborates on the following outline.
CATEGORY A. AQUEOUS SOLUTIONS

A-1 Products derived from alkali silicates. A clear distinction is made between waterproofing gels, where the silicate is very diluted and the reagent is generally mineral, and consolidation gels, for which the silicate is less diluted and the reagent is organic.

A-2 Mineral products other than alkali silicate. (ethyl or methyl silicate, silica and derived products, fluosilicate, alumina, magnesia)

A-3 Lignosulfite or tannin derivatives
A-4 Other plant derivatives
A-5 Acrylamide derivatives
A-6 Phenoplasts
A-7 Aminoplasts
A-8 Combination grouts

CATEGORY B. COLLOIDAL SOLUTIONS

B-1 Organic. (alginate, etc.) (marine algae extracts)
B-2 Mineral. (bentonite, etc.) (mineral treated clays)

CATEGORY C. NON-AQUEOUS SOLUTIONS

They generally have a viscosity too great to satisfy the definition of chemical grout (viscosity 20 cP). However, chemical grouts can be obtained with modifications in the following categories:

C-1 Synthetic resins
C-2 Vulcanizable oils
C-3 Bitumen and other heated compounds
C-4 Systems Containing Solvents

CATEGORY D. EMULSIONS

D-1 Bituminous emulsions
D-2 Other emulsions

CATEGORY E. PRODUCTS REACTING WITH THE GROUND

E-1 Reaction with salts in ground or in groundwater
E-2 Reaction with groundwater

CATEGORY F. COMBINED SYSTEMS
6. Evaluation According to Quality-Price Criteria

We have adopted the following analysis procedure, inspired by the DELPHI method:

1) Determine the list of technical and economical criteria which will take into account all of the products under comparison.

2) Assign a percentage to each of these criteria.

3) Assign a rating by criterion for each of the proposed products.

This evaluation eliminates ambiguity, since the rating is correlated to an economical criterion, where ambiguity might be present with a technical criterion. In fact, ambiguity is often present in bibliographic documents since these technical criteria (physico-chemical characteristics of fresh grouts, mechanical characteristics of hardened grout) are not precisely indicated. And, where this preciseness exists, as is the case for certain suppliers, it is difficult to compare results as operating methods differ from laboratory to laboratory. Therefore, it is clear that in order to be extremely precise in the establishment of a quality-price classification, standard testing should be available for each of the products to be evaluated.

When points of comparison were too scattered because of a lack of bibliographical documentation, the missing values on various criteria were determined in our laboratory.

Seven criteria were determined, with the following ratios (table 1):

1) cost of the product (30%)
2) ease of preparation and injection (10%)
3) effectiveness of treatment (10%)
4) durability of treatment (10%)
5) toxicity during construction (5%)
6) toxicity after construction (15%)
7) independence from petrochemicals (20%)
Table 1. Available Rating Points

<table>
<thead>
<tr>
<th>Criterion</th>
<th>Max % Available</th>
</tr>
</thead>
<tbody>
<tr>
<td>No. 1 Price of material</td>
<td>30</td>
</tr>
<tr>
<td>No. 2 Workability</td>
<td>10</td>
</tr>
<tr>
<td>No. 3 Effectiveness of treatment</td>
<td>10</td>
</tr>
<tr>
<td>No. 4 Durability</td>
<td>10</td>
</tr>
<tr>
<td>No. 5 Toxicity at the time of construction</td>
<td>5</td>
</tr>
<tr>
<td>No. 6 Harmful impact on environment</td>
<td>15</td>
</tr>
<tr>
<td>No. 7 Derivation of principle raw material</td>
<td>20</td>
</tr>
</tbody>
</table>

Criteria 1 and 2 concern the economy of the procedure, the sum of these two terms being 40%. Of this value, the major part concerns the product itself; ease of operation is less important. Thus a ready-mixed product will have a better rating than a grout which must be made up on site of several ingredients. Similarly, when the use of a more viscous product or one which must be injected in two phases leads to greater expense, this product will receive a very low rating in category 2.

Criteria 3 and 4 relate to the immediate and long-term effectiveness of the treatment, the sum of these two terms being 20%. Aside from the parameters directly related to the research goal, other factors will be taken into account: nature of the grout, viscosity, ease with which setting time can be regulated.

Criteria 5 and 6 concern the immediate and long-term risks of the product, the sum of these two terms being 20%. Long-term harmlessness is considered more important than that of immediate, since protection of personnel during construction is relatively simple.

Criterion 7, assigned 20%, concerns the future, and tends to favor mineral or organic products.

When a grout can be used both for waterproofing and consolidation, two different ratings will be established.

All of these ratings are available in the form of a general comparative table at the end of this volume (table 17).
CHAPTER II

CATEGORY A: AQUEOUS SOLUTIONS

1. Introduction

Some non-rigid non-granular aqueous solutions will convert to fairly strong solids under normal temperatures and within a predictable time. These types of aqueous solutions are frequently used for grouting of fine sands. The products in this category are the oldest known and the most often used for grouting fine soils, 90% of chemical grouts formerly and presently in use are in this category A, and are by far the most important of the available grouts. For clarification they are divided into the 8 categories listed below.

Category  A-1  Silicate derivatives
A-2  Other mineral gels (alumina, magnesia)
A-3  Lignosulfite derivatives
A-4  Other plant derivatives
A-5  Polyacrylamides
A-6  Phenoplasts
A-7  Aminoplasts
A-8  Combination

2. Category A-1. Silicate Derivatives

The chemicals used to stabilize a fine soil must fill the voids and bind together the components of the granular skeleton. This operation waterproofs the ground and also consolidates or strengthens it, if the grout is strong. With silica gels, both operations are feasible.

The silicic chains on a tridimensional network have a solid macroscopic structure. This assumes the form of a gel capable of ensuring good cohesion in microgranular ground.
This cohesiveness increases as the diluteness of the grout decreases.

In these silica gels the network's basic atom is silicon. They can thus be prepared from numerous silica derivatives. Among these, water-soluble fluorosilicates precipitate upon contact with an alkaline hydroxide to form a gel (39-12, 40-17, 62-19, 65-18, 68-14, 72-09, 73-04). The silicon esters (ethyl-ortho-silicate), mixed with an alkaline solution, hydrolyze and precipitate in the form of a silica. Organiz derivatives such as methyl silicate gel after a variable interval through the addition of polybasic acids (phosphoric acid, oxalic acid, citric acid). Silicon halides (SiF₄, SiCl₄) introduced into the medium in solution or in the form of gas, can waterproof granular soils (35-12, 65-17).

But the basic products most often used are the alkali silicates (sodium, potassium and lithium) and, more specifically, sodium silicate, which is employed in nearly all ground chemical grouting work.

The alkali silicates are compounds with tetrahedral structures. Silica (SiO₂) is the simplest chemical form. The alkali silicates of sodium and potassium are prepared in tank-kilns, under the following chemical reaction:

\[ n\text{SiO}_2 + n\text{Na}_2\text{CO}_3 \xrightarrow{1,400^\circ C} n\text{SiO}_2\cdot n\text{Na}_2\text{O} + n\text{CO}_2 \]

The vitreous silicates thus formed are treated with water in an autoclave under controlled pressure and temperature conditions, producing colloidal solutions very sensitive to changes in temperature. Alkali silicates are comparable to colloidal solutions of silicic acid in sodium or potassium. Their colloidal nature can be demonstrated by the Tyndall effect (65-04, 52-13, 64-18, 71-01, 99-10). These solutions, characterized by the silica/alkali ratio which varies from 1 to 4, have many industrial applications, acting as adhesives, deflocculants, basic catalysts and as detergent bleaching agents.

The silica/alkali ratio \(n\) strongly influences the properties and, consequently, the applications of silicates, enabling a distinction of two types of silicate:

- detergent action silicates where \(n\) is fairly close to 2;
- adhesive action silicates where \(n\) varies from 3 to close to 4.
It is the second type of silicate which is used for grouting. Several compounds commonly used in grouting procedures are shown below (table 2).

### Table 2: Silicate Compounds Commonly Used in Grouting

<table>
<thead>
<tr>
<th>Baume degrees</th>
<th>Weight ratio SiO&lt;sub&gt;2&lt;/sub&gt;/Na&lt;sub&gt;2&lt;/sub&gt;O</th>
<th>Viscosity cP</th>
<th>% SiO&lt;sub&gt;2&lt;/sub&gt;</th>
<th>%Na&lt;sub&gt;2&lt;/sub&gt;O</th>
<th>%H&lt;sub&gt;2&lt;/sub&gt;O</th>
</tr>
</thead>
<tbody>
<tr>
<td>30-31</td>
<td>3.9 - 4.0</td>
<td>40-50</td>
<td>22.7</td>
<td>5.7</td>
<td>71.6</td>
</tr>
<tr>
<td>30-31</td>
<td>3.87</td>
<td>40-50</td>
<td>23.1</td>
<td>6.0</td>
<td>70.9</td>
</tr>
<tr>
<td>35-37</td>
<td>3.3 - 3.4</td>
<td>60-70</td>
<td>25.8</td>
<td>7.7</td>
<td>66.5</td>
</tr>
<tr>
<td>36-38</td>
<td>3.4</td>
<td>50-100</td>
<td>26.5</td>
<td>7.8</td>
<td>65.7</td>
</tr>
<tr>
<td>38-40</td>
<td>3.3 - 3.4</td>
<td>160-200</td>
<td>27.7</td>
<td>8.3</td>
<td>64.0</td>
</tr>
<tr>
<td>40-42</td>
<td>3.15 - 3.25</td>
<td>200-260</td>
<td>28.7</td>
<td>9.0</td>
<td>62.3</td>
</tr>
</tbody>
</table>

The present tendency in grouting is to use high ratio silicates. Accordingly, the principal manufacturers of sodium silicate have developed low sodium content silicates whose molecular ratios attain 3.9. These silicates, at the uppermost limit of the stability range, are conducive to the formation of a gel. Beyond a ratio of four the silicate is no longer stable.

One means of artificially increasing silica content is the patented COME process (61-18), which consists of adding a micellar silicic anhydride to the silicate. The micellar silicic anhydride forms a chemical compound with the silicate in such a way that setting takes place exactly as if a silicate had been used with an SiO<sub>2</sub> ratio considerably lower than that found in commercial or natural silicates. Regrettfully, the procedure proposed by COME is for a purpose other than grouting and is not applicable to grouting, as its micellar silicic anhydride is much too thick.

#### 2.1 Composition of Silica Gel

The alkali silicates, particularly sodium silicate, play an important role in grouts which are injected into the ground. Once in the ground, the silicates in solution harden through the action of one of several setting reagents, in general, acids, polyvalent cations or specific organic reagents. This method of gelting sodium silicates consists of decreasing the electrical charge, the reaction taking place in two phases:

13
a) Discharge of the silicic ions, which, in the case of an acid gelifying reagent, results in lowering the pH and decreasing the free sodium. This reaction is instantaneous and, during polymerization, the proportion of total sodium will not vary.

b) Polymerization of the silicic ions. The silicic ions, partially discharged, will bind together at the end of a certain interval following Brownian movements. At the same time, the monosilicic and polysilicic ions will polymerize (41-27, 51-17, 55-03, 56-10, 56-14, 65-04, 66-03, 71-01).

The colloidal solution thus converts to a "sol" (silicate plus reagent) after the addition of a reagent and then to a solid or pseudo-solid gel at the end of a variable interval.

The polycondensation of silicic ions proceeds at a pace governed by the amount of reagent in the grout. One can thus monitor changes in the grout's viscosity and determine the time it takes to set, which in turn determines the interval during which the solution can be injected, the setting interval being the amount of time the "sol" takes to turn into a gel. It depends mainly on the amount of reagent added and the concentration of silicate in the solution. Other factors such as temperature, pH, and dilution also affect this parameter (47-05, 62-03, 64-12, 65-03, 65-04, 99-07, 99-09, 99-10).

The polycondensation of the silicic ions leads to a reticulated tridimensional network whose structure was diagrammed previously. This gel structure in the form of a net is characterized by micellar chains and chains of particles. They are connected by hydrogen links and Si-O-Si links. A structure maintained by weak cohesive forces cannot possess the strength of a structure with a crystalline network.

The macromolecular diagram given previously indicates that there is only one water molecular per atom of silicon in the gel; whereas in the sol, the number of water molecules clearly exceeds the number of silicon atoms. In the void spaces in the gel structure, 6 m in size, are also included sodium salts, reagent anions and silicic acid which has not polymerized in the excess of water (65-04, 71-01, 55-03).

Different laboratory studies show that silica gel contracts after a certain time. During this phenomenon, called syneresis, the gel expels free water containing
sodium salts, colloidal silica and gelifying reagent anions in true or colloidal solution. The syneresis phenomenon occurs only in pure gel or in cases where the skeleton is coarse. It does not appear when the gel is injected into fine sands, and the adherence of the gel to a skeleton inhibits its contraction. The other phenomenon to which the gel can be subjected is its dissolution in a great excess of water, which produces a reverse reaction: gel → sol. This reaction can be almost eliminated by sufficiently destabilizing the silicate through a sufficient proportion of reagent (65-03, 65-04, 99-09, 71-01, 99-07, 69-01, 62-17).

The mechanical characteristics of the gel are determined as follows:

a) In a pure state, shear strength depends on the amount of reagent used and the silica concentration in the solution, the silica concentration depending in turn on the dilution of sodium silicate in the gel, as well as the molecular ratio of the silicate used.

This is not a simple relationship, for in a sodium silicate the silica and the sodium are closely linked. The amount of silica likely to be precipitated will be proportional to the amount of sodium neutralized in the first phase of the gel's setting reaction. In other words, if two gels have the same SiO₂ content and the same amount of gelifying reagent, the stronger of the two gels will be the one whose Na₂O content is lower, while the amount of sodium which can be neutralized at the time of formation of the gel is very limited. It is therefore advantageous to use silicates with a low sodium content, that is, with a high molecular ratio SiO₂/Na₂O.

b) In a sand-gel mixture, compressive strength depends on the amount of reagent and on the silica concentration in the solution, and also on the granulometry (coarseness) of the sand injected.

To establish a relationship between the strength of the grouted ground (Rs) and the strength of the pure gel (Rg) is most important but difficult. Various formulas are possible. A simplified one, given by CARON (65-04) is:

\[ Rs = Rg \left(1 + k \sqrt{s}\right) \]

where S is the specific surface area of the sand.
It must be noted, however, that many other factors affect the strength of the grouted soil: rate of compression, mineralogical character of the sand, apparent density of the sand, saturation rate, and others.

Silica gels are generally used for grouting fine sands and homogeneous media having a specific surface area \((S)\) of 100 to 1,000 \(cm^2/g\) and a natural permeability \((K)\) of \(10^{-5}\) to \(10^{-3}\) m/s. Silica gels are also used after other grouts as a complement for the treatment of coarser alluvial deposits.

Waterproofing is achieved through the use of soft gels with weak mechanical properties, consolidation procedures through the use of hard gels. In general, the silica gels used for grouting have frequently been studied and are referenced below:


This long list is not definitive, and references are included later in this text. The abundant literature on grouting with silica gels shows that this method has been and continues to be highly successful.

2.2 Silica Gel Grouting Procedures

In 1886, for the first time, a German patent (JEZIORSKY) recommended the use of a silica gel to fill voids in the ground. Since that time, many procedures have been suggested and some of them have enjoyed extensive application.

This first method calls for separate injections of the silicate solution and the reagent in the medium to be consolidated. This technique was widely used and quite successful, but is rarely used today.
A later method calls for a one-shot injection of a mixture which will set at the end of a predetermined interval. This method was first used for waterproofing. The appearance of organic reagents, in 1957, led to important results in the field of sand consolidation.

2.21 Separate Injections of Alkali Silicate Solution and Reagent

An alkali silicate solution with a high silica content and a mineral reagent in a concentrated solution are injected successively into the medium to be treated. The chemical change, sol → gel, takes place almost instantaneously when the silicate and the reagent meet in the ground.

A. The Joosten-Jeziorsky Process

The idea of consolidating porous ground with a silica gel dates back to JEZIORSKY (00-01). However, it is to JOOSTEN that we owe the first successful application of this principle. The JOOSTEN process consists of injecting a concentrated solution of sodium silicate (37-38°Be) and a calcium chloride solution (35°Be) separately into the ground. The reaction, which takes place immediately, gives a strong gel which ensures good consolidation in the grouted ground. This method has been widely adopted for the consolidation of loose, weak soils whose permeability exceeds 10^{-4} m/s. Further, the strength of the treated sands varies from 20 to 80 kg/cm² (64-12). However, DEBECQ asserts that he has obtained the following strengths in situ (49-03):

- on fine sands: from 10 to 40 kg/cm²
- on gravels: from 40 to 100 kg/cm²

These results are in contradiction with laboratory tests which tend to prove that the best compression strengths are obtained in the finer granular skeletons.

The gel formed is very resistant to water erosion and chemicals. The reaction can be expressed as follows:

\[ \text{Na}_2\text{O} \cdot \text{SiO}_2 + \text{CaCl}_2 + \text{H}_2\text{O} \rightarrow \text{Ca(OH)}_2 + \text{SiO}_2 + 2 \text{NaCl} \]

Although calcium chloride is the compound most frequently used, it is not the only possible reagent. MILLS suggests magnesium chloride (22-01).
Various improvements on the JOOSTEN process have been made. The alkalinity of a silicate solution can be increased through the addition of an alkaline carbonate or hydroxide (40-28). This procedure serves the purpose of improving the grout's penetrability.

The GUTTMAN process uses sodium carbonate which, when mixed with the silicate solution, decreases its viscosity and thus improves its penetrability. Once the silicate-sodium carbonate mixture has been injected into the medium to be treated, calcium chloride is introduced (38-13, 50-02, 57-07, 58-04, 62-13, 63-07).

HODGSON also suggests a two-shot injection. First, a MeCl$_2$[1] mixture —sodium or potassium— is introduced into the ground. The MeCl$_2$ precipitates in the form of Me(OH)$_2$, but does not harden. Then, sodium silicate is injected and gives cohesion to the terrain. This procedure is particularly suited to fine soils (48-16, 63-08, 73-02).

Despite these improvements, the Joosten process has the following disadvantages:

a) The high viscosity of the solutions, due to the highly concentrated nature of the products used, limits their penetrability in fine sands and necessitates injections under high pressure.

b) The short range of the two compounds must be compensated for by many close-set bore-holes.

c) Finally, one cannot control the silicate-reagent mixture in the ground. Thus complete gelification is not assured (49-03, 56-07, 62-11, 62-28, 63-02, 70-05).

Various patents and publications have helped to identify the advantages and disadvantages of the Joosten process: (27-03, 27-01, 28-03, 31-04, 32-03, 33-03, 35-03, 36-04, 36-06, 36-20, 36-02, 37-06, 38-09, 38-10, 39-01, 41-03, 41-04, 49-05, 50-01, 50-02, 50-10, 52-02, 52-03, 52-04, 53-01, 54-05, 55-02, 55-09, 57-02, 57-14, 58-02, 59-05, 61-05, 62-13, 62-19, 63-08, 73-01, 32-09, 33-04, 39-23).

[1] Me = Metallic ion
Since 1927, the JOOSTEN process has been used successfully many times throughout the world for various soil consolidation and waterproofing operations. There are many examples in the fields of railroads, (tunnels, bridges, etc.), and mines; but also in urban areas (consolidation of foundations, subways) and in rural areas (bridges, dams). Some of the projects where the Joosten process was used successfully are described in the following:

- in Germany

- in the United Kingdom
  33-02, 33-07, 34-04, 35-03, 35-04, 36-17, 38-07, 39-02, 40-04, 44-02, 49-03, 58-04, 63-07;

- in the U.S.A
  37-05, 37-15, 38-04, 41-05, 41-07, 42-01, 42-02, 43-04, 45-02, 45-03, 47-03, 49-03, 49-06, 49-11, 49-13, 51-05, 54-02, 56-01, 56-03, 57-03, 57-07, 58-13, 57-04, 64-08;

- in the Soviet Union, Poland and Romania
  36-03, 37-09, 39-01, 56-02.

The difficulty of implementing this process explains why it was abandoned in favor of processes which were less costly and more effective.

B. The Francois Process

Patented in 1911 (11-01), this process recommends the use of silica gel in the sealing of fissured ground, the role of the gel being to prepare the ground to receive a cement grout. Later on, the use of gel alone was extended to the waterproofing and consolidation of granular soils.

The FRANCOIS process specifies separate injections of sodium silicate and a concentrated solution of aluminum sulfate. The injections can be made simultaneously in two
neighboring holes. Unlike the JOOSTEN process, this process permits the use of a highly dilute silicate solution, up to 30 to 40 g of dry matter per litre according to the directions. Gelification in the ground is instantaneous. This process has the same disadvantages of execution as the JOOSTEN process (22-02, 38-10, 49-03, 49-05, 54-05, 61-05, 62-13, 62-16, 65-04, 64-12, 50-01), although various operations have been carried out throughout the world with good results (29-06, 30-12, 32-06, 34-03, 37-12, 38-03, 38-09, 40-05).

C. Processes Using a Gaseous Compound

Different gases have been suggested for use as gelifying reagents alone or in combination with other products. The gas can penetrate even the finest pores and thus achieve better cohesion of the ground. The idea is to neutralize the sodium in the silicate by use of a gaseous compound soluble in water. The simplest, carbon dioxide ($CO_2$), was suggested very early, then taken up again by ANDRESEN (46-07).

Many authors thought of introducing a mineral reagent into the ground along with the gaseous compound. JORGENSEN recommended injecting an alkali silicate, then calcium chloride in combination with carbon dioxide (35-13). JOOSTEN recommended the introduction in granular ground of $CO_2$ after the silicate and the electrolyte salt ($CaCl_2$) (31-17, 31-19). In 1937, JOOSTEN suggested successive injections in the ground of a metallic sodium-salt-silicate mixture stabilized by ammonia in solution and the gaseous compound $CO_2$ (37-20). He asserted that this method ensured the treatment of fine sands. First, the ammonia prevents gelification, then when the gas reaches the mixture, the ammonia is driven off and the coagulating gaseous compound causes the mass to set. JOOSTEN recommended the following mixture:

- 85 kg of sodium silicate at 38° Baume
- 1.70 kg of ZnCl$_2$
- 7.93 kg of water
- 1.13 kg of sodium
- 4.24 kg of ammonia liquor

The reaction between the silicate and the gas can be expressed as follows:

$$Na_2O\cdot xSiO_2 + 2CO_2 + nH_2O \rightarrow xSiO_2\cdot (n-l)H_2O + 2NaHCO_3$$

Various documents contribute to a better understanding of alkali silicate gelification through the use of carbon dioxide (49-07, 31-07, 57-15, 58-07, 58-14).
However, CZERNY, REGELE and SCHWOY assert that the gel thus obtained is unstable in water and that ground stabilization proves ineffective if particles finer than 0.06 mm compose more than 20% of the soil by weight (69-07). They also suggest submitting the alkaline silicate to the action of a fluorinated gas for purposes of waterproofing or consolidating soils.

The gaseous mixture composed of fluorosilicic acid \((\text{H}_2\text{SiF}_6 \cdot x\text{H}_2\text{O})\) and hydrofluoric acid \((\text{HF})\) can be obtained through the action of sulfuric acid on the sodium fluorosilicate \((\text{Na}_2\text{SiF}_6)\) (67-10). The action of these acid compounds on the sodium gives by-products \((\text{NaF}, \text{Na}_2\text{SiF}_6)\) which are only slightly soluble in water. In addition to the gel formed, they contribute to a plugging effect. In the same spirit, ZEMLIN advocates hydrofluoric acid (31-16) and MULLER, chlorine (31-14).

2.22 Single Phase Grouting Procedures for Waterproofing

The silicate solution and reagent mixture is prepared before proceeding with the injection. Such a procedure is much less costly than any two-phase process. In effect, the two compounds are injected at the same time through the same grout-hole.

The more practical one-shot injection is by far the most frequently used today, producing either plastic gels intended to waterproof sands or gels with strong mechanical properties which ensure good cohesion in the treated ground.

A. Choice of Reagent

A dilute sodium silicate solution sets at the end of a predictable interval through the use of small amounts of acids or mineral salts. Many procedures have been suggested and some have given interesting results. Among the first patented monophase systems were the LEMAIRE and DUMONT process which specifies the use of a mineral acid as a coagulating agent (09-01) and the FRANCOIS process using a sufficiently dilute alumina sulfate solution (11-01). The first real use of the procedure was about 1930 with the construction of the Bou-Hannifa Dam, using the RODIO process.

A.1 Acids and Acid Salts

The concept of gelling an alkali silicate with an acid can be traced back to LEMAIRE and DUMONT (09-01). The mineral acid in dilute solution decreases the pH in the medium and thus favors the formation of aqueous silicic acid. The
setting reaction leads to an aqueous gel with the following general formula (57-06):

\[ \text{SiO}_n(\text{OH})_{2n-4} \]

Various authors have studied the action of mineral acids on a solution of alkaline silicate (22-01, 48-03, 40-10). The mixture's setting time can be regulated by varying the ratio of the two compounds. REIMERS studied the following proportions (43-17):

- 8 to 16% by weight of sodium silicate
- 4.7 to 20.5% by weight of sulfuric acid

The nature of the acid can vary. Within the range of strong acids, besides hydrochloric acid and sulfuric acid, which have already been mentioned, a place of honor must be accorded to phosphoric acid (63-12). However, weak acids and acid salts are generally preferred, the most widely used being sodium bicarbonate, sodium tetraborate, sodium bi-sulfate and monosodium phosphate.

One prepares solutions with low initial viscosity and variable setting intervals. For the sodium silicate-sodium bicarbonate mixture, the initial solution can be varied:

- initial viscosity: 1.5 cP
- time of set: from 0.1 to 300 min
- density: 1.02 (63-06)

ANDRESEN (44-17) recommends two successive injections:

1. a dilute solution of sodium silicate and sodium bicarbonate with a setting time of 10 to 20 hours;

2. then a second, more concentrated, solution with a setting time of 6 to 8 hours.

Various works contribute to a better definition of these different methods (50-02, 51-18, 54-05, 55-04, 63-02, 63-08, 62-17, 64-12, 65-04, 72-04, 73-04, 99-12).

A.2 Ammonium Salts

According to this procedure, an ammonium salt is used as a coagulating reagent. In 1936, JOOSTEN mixed a heavy metal salt and an ammoniacal colloid with sodium silicate (36-20). LAWTON added only a weak base or the salt of a weak base to an equeous silicate solution (40-20). Thus, ammonium hydroxice, or ammonium sulfate, chloride, or nitrate can bring about gelification of the silicate. Ammonium acetate or citrate can also be used. The chemical
reactions of the conversion are as follows:

\[
\begin{align*}
(NH_4)_2SO_4 & \rightarrow 2NH_4^+ + SO_4^{2-} \\
2NH_4^+ + 2H_2O & \rightarrow 2NH_4OH + 2H^+ \\
2H^+ + Na_2SiO_3 + H_2O & \rightarrow Si(OH)_4 + 2Na^+
\end{align*}
\]

Two mixtures with different setting times can be used as examples:

1) -10 parts by volume sodium silicate (15.2% silicate by weight)
   -3.5 parts by volume ammonium sulfate (10% by weight)
   Setting time: 14 min.

2) -10 parts by volume sodium silicate (15.2% silicate by weight)
   -2.5 parts by volume ammonium sulfate (10% by weight)
   Setting time: 5 hours (40-20)

This method does not seem to have enjoyed much success with grout users (49-05, 63-08, 63-20, 63-02).

A.3 Polyvalent Salts

Some authors have suggested the use of a polyvalent salt to coagulate alkali silicates. Thus, magnesium and calcium sulfates and carbonates, as well as ferric and aluminum chlorides can be used as coagulating reagents (40-13, 56-11, 58-08, 59-11, 60-07, 60-10, 63-16, 65-07, 63-15, 60-11).

WILLIAMS studied the action of an alkali silicate in an aqueous medium containing a metallic compound (66-04). The compound is composed of a metallic ion (Ba, Ca, Mg, Cu, Al ...) and a compounding agent (di- or tricarboxylic acid or sodium phosphate). The gel's setting time will relate to the solution's pH factor. However, these different procedures have not been applied on a large scale.

B. The Rodio Process

This is without doubt the first monophase process to have enjoyed some interesting applications. RODIO suggested the addition of milk of lime to a dilute solution of sodium silicate. Following an exchange of bases, a sol is formed of calcium silicate, with variable setting time.
C. Use of Sodium Aluminate as Reagent

In 1938, VAIL suggested the use of sodium aluminate as a coagulant (38-12). This compound (Al₂O₃ · Na₂O) mixes perfectly with a sodium silicate solution thanks to the amphoteric nature of aluminum. As soon as the reagent is added to the solution, an insoluble aluminum silicate is formed. One thus obtains a uniform gel at the end of an interval which can be regulated by varying the pH and the dilution of the medium. Sodium can be added to such a solution with a low viscosity. The results obtained are satisfactory.

Setting time: from 1 min to one hour

Compressive strength of the sand treated: several kg/cm²

This process is suitable for waterproofing sands, making possible the reduction of the permeability of the ground from 10⁻⁵ to 10⁻⁷ m/s (56-06, 56-07). This method's inherent possibilities have led many authors to study it (43-05, 50-02, 50-20, 52-02, 55-08, 54-05, 63-07, 61-05), and applications of this process are promising (64-21, 65-03, 65-13, 65-14, 49-04, 55-08, 62-11, 73-04).

D. Combined Procedures Using an Acid and a Heavy Metal Salt

One can prepare low-viscosity grouts composed of a mixture of sodium silicate solution, mineral acid and heavy metal salt. In 1941, LANGER (41-10) suggested such a mixture for the treatment of fissured rock, powdery soils and to restore masonry. As an illustration he recommended the following grout:

- 2 parts silicate (50%) at 36°B
- 1 part salt and acid mixture

The acid and the salt most frequently used are hydrochloric acid and copper sulfate. However, iron, zinc and lead salts are equally suited to such a process. The role of the acid is to lower the pH factor of the silicate solution. The strong coagulating reagent is then the salt (37-16, 47-09, 48-22, 54-05, 61-05, 62-13, 62-17, 62-28, 63-08, 65-04).

Various applications of this technique have demonstrated its success. For example, it has been used on the
Bou-Hannifa Dam in Algiers (38-03), the Neuilly Bridge (near Paris) (37-11) and for consolidation of foundations for floodlights at Kezar Stadium, San Francisco, California (49-01). Other references (37-11, 39-05, 39-06) are available on this subject.

In this technique, based on the REIMERS patent (42-06), the acid necessary for the combined reaction is created by electrolysis. Since this takes place internally, this process is limited to grouting through bore-holes with metal tubing.

In another procedure using combined reagents, GAYRARD recommends treatment of the area by injection of the following mixture:

- sodium silicate
- alkali bicarbonate: 3 to 15% of the silicate by weight
- sodium chloride: 3 to 15% of the silicate by weight
- sodium or potassium hypochlorite: 0.3 to 1% of the silicate by weight

The exact proportion of each component is adapted to the characteristics of the ground, however it is preferable to choose silicates with a density of 3.3, and a weight ratio of 3.5, diluted in nine times their volume of water (31-20, 49-03, 61-05, 61-08, 65-04, 50-01). In its primitive form, the GAYRARD process was never used in any large construction work.

LERCH, MATHIS and GATCHELL suggest the following mixture:

- one part diluted silicate
- one part aqueous solution:
  3.5 parts HCl (Hydrochloric acid)
  19 parts sodium bisulfate (41-14)

In the Soviet Union, the mixture HCl + Al₂(SO₄)₃ has been used as a coagulating reagent. The silicate-reagent mixture has a viscosity of about 1.7 cP and solidifies at the end of a variable interval (60-09, 62-13).

2.23 Single Phase Grouting Procedures for Consolidation

The various one-shot procedures mentioned previous-
ly produce gels whose setting interval can be regulated. However, these gels are soft and suitable only for water-proofing. Therefore, one-shot hard gels had to be developed.

Most of the reagents used to obtain a gel with strong mechanical properties are organic compounds. However, these products are not the effective coagulating agents. They react with the water-silicate mixture to release an acid or a compound which in turn acts as an acid which neutralizes the colloidal matter and causes the grout to set.

A. Aliphatic Esters

In 1957, C. CARON described a new method for coagulating alkaline silicates which would use compounds acting as acids, or which would release an acid, as coagulating agents (57-17, 61-19). This method produces a strong gel whose setting time can be easily regulated, thus permitting the consolidation of sandy ground. In his original patent, C. CARON suggests the following mixture as an illustration:

- 99 parts by volume of sodium silicate at 36°B
- 10 parts by volume of ethyl acetate
- 1 part by volume of Teepol (tensio-active detergent)

This grout sets in 50 minutes and, after 24 hours, the pure gel will have a compressive strength of 20 kg/cm². To this mixture a tensio-active material (Teepol) is added, causing emulsification of the reagent in the alkaline silicate solution.

The ester is subjected to hydrolysis, resulting in an acid and an alcohol. The first compound formed is the true coagulating agent, the alcohol contributing to coagulation by dehydrating the medium.

\[
\text{CH}_3\text{-C}-\text{O}-\text{C}_2\text{H}_5 + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{-C}-\text{OH} + \text{C}_2\text{H}_5\text{OH}
\]

ethyl acetate \hspace{1cm} \text{acetic acid} \hspace{1cm} \text{ethanol}

Ethyl acetate is not the only ester which has been suggested. One could also use:

- glycerol triacetate (triacetin)
- ethyleneglycol diacetate
- butyrolactone
- ethyl formate
- ethyl oxylate
-diethylsuccinate and dimethyl succinate (65-20, 71-02)
-and others (65-15, 61-23, 64-19)

In order to increase the solubility of the ester in the sodium silicate, it has been suggested that a third solvent be added to improve the mixture's homogeneity (formamide, dimethyl formamide or urea). It is preferable to use a formamide which has a certain hardening property. As an illustration, the grout would be as follows:

-62 g glyoxal tetra-acetate in 300 g of formamide (98% solution), brought to 1000 cc with water
-10 parts this solution
-100 parts sodium silicate solution

density = 1.21
molecular weight ratio $\text{SiO}_2/\text{Na}_2\text{O} = 5$

In addition, this gel is resistant to erosion by water, registering losses under intense flushing by water of:

-nothing at the end of an hour
-1.25% per hour after 2 hours
-0.17 per hour after 21 hours

At present, the process using esters as coagulating reagents seems to be the most commonly used for the consolidation of fine sand and there is abundant literature on this topic (99-09, 73-06, 70-05, 73-04, 63-07, 65-04, 73-02 63-03, 63-08, 64-12, 70-04, 73-01, 67-04, 72-11). This process has been used at numerous construction sites, including the following:

-excavation protection in Montessuy, France (65-03)
-Paris Area Rapid Transit System:
  -St. Augustin- Hausmann- Auber- Opera- Capucines District (73-04)
  -Auber Station (70-04, 67-04, 72-12)
  -East-West Line, Defense- Neuilly segment and the passage under the Seine (67-04, 70-05)
-Munich subway, Lot Harras (72-02)
-Vienna subway, Austria (72-02)
-excavation protection, Wuppertal, West Germany (65-03, 63-07)
-Saint-Denis-Acheres outlet, Argenteuil, France (65-03, 64-12)
-Fessenheim electric plant, Alsace (64-12)
- Blackwell highway tunnel under the Thames, Great Britain (65-05, 67-04)
- Foundations for the new hydroelectric plant in Fissingen, Bavaria (67-04)
- Neuilly Bridge foundation protection, Paris (65-04)
- Printemps Department Store foundation (65-03)
- Notre Dame de Commiers Dam on the Drac, France (65-12, 62-18)
- Spanish National Railroads, Plaza de las Glorias junction, Sagrega (72-02)

B. **Aldehydes**

In 1958, GANDON, LEHMANN, MARCHEGUET and TARBOUR-IEGH suggested the introduction into the ground of a grout composed of an aqueous solution of alkaline silicate and an aldehyde (58-10). Aldehyde function compounds, which are capable of coagulating the grout, should not have H in alpha in the grouping $-\text{C}-$. Theoretically, then, one can use:

- formaldehyde, glyoxal, benzaldehyde, furfural and trimethylacetaldehyde, although at room temperature, only glyoxal seems to be appropriate. If the compound is not heated, the speed of its reaction is too slow using the other aldehydes mentioned. As an example, the following grout sets in 30 minutes and becomes a hard gel at the end of an hour:

  - 10 parts by weight of an aqueous solution of sodium silicate at 36°B ($\text{SiO}_2/\text{Na}_2\text{O} = 3.4$)
  - 1 part 30% neutral glyoxal solution.

By Cannizaro reaction, the aldehyde converts to an acid and an alcohol.

$$2H-C-C-H \xrightarrow{\text{NaOH}} HO-C-C-OH + CH_2OH-CH_2OH$$

Glyoxal Oxalic acid Ethyleneglycol

To the silicate-glyoxal mixture can also be added an organic accelerator of the following type (67-05, 62-27, 65-15, 64-12, 65-04, 67-04):

$$R-C-R, R-O-R, O\overline{\text{R-O}}$$
C. The Amides

Among the different amides, only formamide is really used as a coagulating agent. In 1959, PEELER first recommended the use of an amide (59-15). Generally, formamide constitutes 2 to 30% by volume of the grout, whose setting time can vary from 5 to 300 minutes (61-22, 63-06). The amide in solution in the medium undergoes hydrolysis. The ammonium salt reacts with the sodium in the solution, causing the grout to set by releasing ammonia:

\[
\text{H}_2\text{C-NH}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{C-O}^-\text{NH}_4^+
\]

One can also add mineral or organic accelerators to the silicate-formamide mixture (65-15, 67-09, 63-06, 65-04, 64-12, 73-01, 67-04):

- mineral: \(\text{CuSO}_4; \text{CaCl}_2; \text{ZnCl}_2; \text{NaHCO}_3; \text{AlCl}_3; \text{Al}_2\text{O}_3; \text{Na}_2\text{O}\)
- organic: \(\text{R-C-R}; \text{R-O-R}; \text{O}<\text{R}<\text{O}\) (67-05)

D. Acid Chlorides

In 1959 SCHMIDT and GEDENK studied the following mixtures:

- alkali silicates- acid halogens
- alkali silicates- acid anhydrides

They also suggested the addition to this mixture of a catalyst (0.1 to 1% by weight): alcohol, alcoholate, ketone. This catalyst permits effective control over the setting time. Acid chlorides are the most commonly used, undergoing the following hydrolysis:

\[
\text{R-C-Cl} + \text{H}_2\text{O} \rightarrow \text{R-C-OH} + \text{HCl}
\]

As an illustration, a gel can be prepared with strong mechanical properties and a setting time of 90 minutes (59-02, 65-04, 61-24, 61-25):
- 500 cc sodium silicate at 38°B
- 480 g Na₂O/l
- 1600 g SiO₂/l
- 1500 cc water
- 38.6 cc acid chloride
- 20.0 cc emulsifier (sodium salt)
- 5 cc catalyst (methyl-glycol)

2.3 Advantages and Disadvantages of Silica Gels

2.3.1 Technical Advantages

a. Control of Setting Time

Setting time depends on the nature of the silicate (dry extract ratio), on the sodium silicate's concentration, the nature of the coagulating agent (figures 1 and 2) (44-04) and temperature (figure 3) (65-04).

For all these parameters, it is possible to draw up charts which define setting times with precision. If these intervals are deemed too short or too long, it is possible to modify the nature of the coagulating agent or to combine it with other accelerating or retarding agents. It is thus possible to obtain any desired setting time, from a few minutes to several hours, and within a broad temperature range. Some examples are shown in figure 4 (99-09).

b. Control of Strength

Unconfined compressive strength depends on the nature (ratio and density) of the silicate used, on the concentration of silicate in the grout, on the concentration of the setting agent in the grout, on temperature and the length of time the grout has cured. As is the case for setting time, it is possible to establish formulas and plot charts for these different parameters which define perfectly the projected strengths, which can vary from a few bars to nearly 100 bars. For example, CARON suggested the following formula for pure gels (65-04):

\[
R = \frac{f(c)}{1 + bt}
\]

where:
- \( R \) represents the pure gel's shear strength in g/cm²
- \( c \) the concentration in sodium silicate expressed in cm³ per litre of gel
- \( b \) a coefficient depending on the nature of the reagent
- \( t \) setting time in minutes.
Composition of reagent:
copper sulfate dissolved in 92.5% water and
7.5% hydrochloric acid
temperature of test: 70°F

Fig. 1. Effect of Copper Sulfate Reagent on Setting Time of Sodium Silicate

University of California
Division of Civil Engineering
MILOS POLIVKA (44-04)
Composition of Reagent:

6.6% sodium bicarbonate
Solution (6.6 G per 100 ml of water)

silicate grade "N" 50% solution by weight

Fig. 2. Effect of Sodium Bicarbonate Reagent on Setting Time of Sodium Silicate

University of California
Division of Civil Engineering
MILOS POLIVKA (44-04)
Fig. 3. Effect of Temperature on Setting Time of Sodium Silicate

CLAUDE CARON (65-04)
Fig. 4. Regulation of Setting Time of Sodium Silicate
Figs. 5, 6, and 7 (44-04) show the effect of the above mentioned factors on shear strength of pure gels. However, since silica gels are viscoplastic compounds, the value obtained for shear strength will be strongly influenced by the speed adopted for the measurement.

In order to predict the strength of the treated ground, a standard sand with clearly defined gradation and compaction should be used as a reference (99-09). With regard to the unconfined compressive strength of sand-gel mixtures, the same reservations apply as for the shear strength of pure gels. Since the material is viscoplastic, its strength will depend on the speed of the press (76-01). Thus, working from strength plotted on a graph for the gel-sand standard, it is possible to determine strength of a grout in the ground itself with some accuracy by using one of the following formulas (99-09):

a.  \[ R_t = R_r - 24.1 + 11.4 \log S_s \]
   where \( R_t \) is unconfined compressive strength of treated ground, bars
   \( R_r \) is unconfined compressive strength of standard sand, bars
   \( S_s \) is specific surface area of the terrain, \( \text{cm}^2/\text{g} \).
   This formula has been tested on silicic terrain for strengths of 6 to 30 bars and soils with specific surfaces from 10 to 250 \( \text{cm}^2/\text{g} \).

b.  \[ R_t = R_r - 11.5 - 5.1 \log K_t \]
   where \( K_t \) is the permeability of the terrain in cm/s.
   This formula has been tested on silicic terrain for strengths of 6 to 30 bars and permeabilities from 3 to \( 10^{-3} \) cm/s.

It can thus be noted that setting time and strength, the two most important factors in grouting, are perfectly controllable.

2.32 Economic advantages

The price of a waterproofing gel will be about the same as a bentonite cement grout, and the price of a consolidation gel will be 2 to 5 times as much. These are the best products to be found at present in the range of conventional grouts.

2.33 Disadvantages

The first drawback is encountered with the consolidation gels. Although their instantaneous strengths are perfectly predictable and adjustable through variations in their composition and in conformity with the above mentioned charts and formulas, their slow crushing strength is much
Amount of Silicate used: 55% volume of voids
30% calcium chloride solution injected in
sufficient amount to solidify 3 X 6 in.
specimens completely

Curing Conditions:
temperature 70°F
relative humidity 50%

Fig. 5. Effect of Silicate Grade on Compressive
Strength (Monterey Sand)

University of California
Division of Civil Engineering
MILOS POLIVKA (44-04)
Fig. 6. Effect of Dilution of Silicate Grade "N" on Compressive Strength of Antioch Sand 0 to No.28

University of California
Division of Civil Engineering
MILOS POLIVKA (44-04)
NOTE:
Amount of silicate used: 55%
volume of voids
30% calcium chloride solution
injected in sufficient amount
to solidify completely
3 x 6 in specimens
Dry curing temperature: 70°F
Relative humidity: 50%

Fig. 7. Effect of Calcium Chloride Concentration on Compressive Strength of Monterey Sand 0 to 14
(Dry Cure)

University of California
Division of Civil Engineering
MILOS POLIVKA (44-04)
lower and less predictable (76-01). This important point, attributable to the visco-plastic nature of silica gels, will be dealt with in detail in the section on standardization. The two other drawbacks, syneresis and leaching, relate to both waterproofing gels and consolidating gels.

Syneresis is not a real problem if the injection is carried out according to the rules, and the grout is well adapted to the gradation of the ground to be treated. If the soil is coarse, a preliminary injection of cement should fill the biggest voids and then one can proceed as for fine ground. The second drawback, leaching, is inherent in the nature of the gel as shown by H. CAMBEFORT and C. CARON (57-13). These authors showed how to limit leaching erosion by using proper setting reagents. There will be some environmental impact no matter how slight this leaching erosion may be, even if it does not affect the permeability or the strength of the ground treated. The salts expelled from the gel by occasional syneresis or leaching are essentially sodium which is not toxic, but its presence in underground water or in the form of an efflorescence in tunnels or basements can constitute a nuisance.

2.4 Rating

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[+] see table 1

Since the ratings for Category A-1 are the first to appear in this text, this is an appropriate place to describe the rating criteria.
Criterion 1: Price of the product

An examination of all the grouts suggested for injection purposes indicates that silica gels, whether those used for waterproofing or those used for consolidation, are the least costly. For this reason silica gels were used as a point of reference, and were assigned a rating of 8, close to the maximum, for both watertightness and consolidation.

A waterproofing gel naturally costs much less than a consolidation gel because of dilution, so this rating is not hard and fast. It simply signifies, in the category in question, how a given product rated in comparison.

Criterion 2: Workability

This second criterion also enters into the price of a product, and mainly concerns the ease with which it can be worked. A syrupy product is less practical to handle than a powder or a true liquid; similarly, in cold weather, sodium silicate risks crystallizing. For criterion 2, silica gel has been assigned an average rating of 6.

Ratings close to 10 are used for products in powder form or liquids which are slightly viscous. Low ratings are assigned to those products requiring extra handling, such as two-shot injections or those requiring a preliminary injection into the ground.

The rating in a given category is quoted for the most practical product, i.e. the best performer in the category in question. Thus, for silicates the rating of 6 is for gels injected in single phase procedure. By these standards, the two-shot Joosten process would have a rating of close to 0 under criterion 2.

Criterion 3: Effectiveness of treatment

According to all the data in the literature and numerous work site references, it appears that silica gels are totally effective for waterproofing and for consolidation. Their rating of nearly 10 is justified by the dependability of their performance. The rating was lowered by one point for waterproofing gels and three points for consolidation gels to take into account the viscosity of the products used, a property which is definitely more pronounced in the case of hard gels than in that of aqueous resins. In fact, because of this viscosity, some fine soils run the risk of poor treatment by use of hard silica gels.
Criterion 4: Durability

Numerous construction site reports prove that areas treated with silicates have not lost their watertightness and strength characteristics after some time. However, as some doubt remains with regard to leaching, the rating of 8 is given for waterproofing gels. In addition, as there are some doubts as to long-term strength, a rating of 7 is given for consolidation.

Criterion 5: Toxicity at the time of construction

In the case of mineral reagent waterproofing gels, toxicity at the time of construction is zero (rating: 10), however there is a slight problem in the case of organic reagent hard gels (rating: 8).

Criterion 6: Harmful impact on environment

Because of the release of a certain amount of sodium, only an average rating of 7 is given.

Criterion 7: Derivation of principal raw material

This criterion mainly concerns petrochemical derivatives whose rating will be close to 0. Sodium silicates are not of petrochemical origin, but the energy required for their manufacture has led to a rating of 8.
3. CATEGORY A-2: OTHER MINERAL GELS

3.1 Introduction

Parallel to the development of silica gels, it was possible to obtain other gels, such as alumina or magnesium oxide, which were injected in one or two phases. All these procedures were used some thirty years ago, while drilling for gas or oil, to plug up cavities in the surrounding terrain and stop water seepage.

3.2 Products

DUNN (39-17) obtained a magnesium oxide precipitate by a two-shot injection: first, of an aqueous solution of magnesium chloride, and then sodium hydroxide. The watertightness obtained with this method was reportedly excellent.

GREBE (39-13, 39-14) preferred to inject a fatty acid salt with a metallic salt. He used either a soap of cocoanut oil which was 40% by weight of potassium salt, (or sodium stearate) with a 20% trisodium phosphate solution, or a 40% potassium salt soap of cocoanut oil with a 4% sodium aluminate solution. It is recommended that pressure be maintained after injection until complete set.

To avoid the premature formation of a precipitate, CHAMBERLAIN (41-15) used as a "stabilizing agent" an organic acid such as lactic, glycolic, or citric. He sees two possible applications,

1. Where the soil is chalky or the water is naturally alkaline. He injects a 2 to 5% solution of metallic salt: iron, antimony, bismuth, tin, cadmium, magnesium, etc., or a non-aqueous solution (alcohol, acetone miscible in water) with the solution containing the stabilizing agent.

2. Where the soil is neutral, as with sands. He adds an alkaline solution of sodium or potassium.

As an illustration, he takes a 2% solution of ferric chloride and an alkaline solution containing lactic acid. The presence of the stabilizing agent raises the pH from 2.7 to 4, at which point the metallic salt precipitates, thus delaying and intensifying the precipitation.
WILLIAMS (43-18) obtained a gel which can be redissolved, if necessary, with a 5% hydrochloric acid aqueous solution. He obtains a gel from an aqueous solution of a metallic salt (aluminum, calcium, chromium, copper) mixed with a phosphate or an arsenate. He cites the following examples of different compositions:

- chromium acetate plus disodium hydrogen arsenate
- chromium acetate plus disodium phosphate
- sodium hexametaphosphate plus ferrous sulfate
- sodium hexametaphosphate plus zinc sulfate
- sodium hexametaphosphate plus manganese sulfate

WILLIAMS suggests injection at a depth of 1500 meters where the temperature is about 60 degrees F. The product takes 45 minutes to reach to bottom, then the precipitate takes an additional 45 minutes to form (application clearly for oil well drilling only).

3.3 Disadvantages

The procedures in Category A-2 offer none of the advantages of the silica gels although their formation proceeds from the same principle. With these mineral gels, the regulation of the setting time is very uncertain, and no method has been developed for consolidation. In fact, very little is known about their performances. DUNN (39-17) has indicated that a gel of magnesium hydrate constitutes a good ground waterproofing agent, but nothing is known of the stability of such a mixture.

Thus, an examination of the products in Category A-2 indicates only the possible future use of residues of mineral industry effluents in grouting (magnesium, phosphorous, aluminum, salts, etc.). But this method could not be widely applied, nor is such a grout "classifiable."

3.4 Rating

For the reasons cited above, no rating has been assigned to this category which is too little known and uniquely specific to certain environmental problems.
4. CATEGORY A-3: LIGNOSULFITE DERIVATIVES

4.1 Introduction

A lignosulfite grout's principal ingredients are lignosulfonate (or lignosulfite) and a hexavalent chromium salt which form a gel through the action of a catalyst.

Lignosulfonates are by-products of wood-processing industries: the manufacture of paper, synthetic fabrics, and wood hydrolysis for obtaining sugars that can be converted to alcohols and various products. Consequently, lignosulfonate is not a clearly defined product. Therefore, for the grout user, the origin and treatment of lignosulfonates are of essential importance for the success of the work. It is therefore necessary to specify the nature of lignosulfonates.

4.2 Nature and Characteristics of Lignosulfonates

In addition to cellulose, wood always contains, in varying degrees depending on species, age and origin: lignin (25 to 35%), hemi-celluloses, glucosans, pentosans, pectic matter, and occasionally tannins, coloring matter, fatty matter, waxes, resins, essential oils and various nitrogenous matter. Lignosulfonates are derived from lignin and constitute a major by-product. It is estimated that 1,000 tons of lignosulfite (raw lignosulfonate), long considered a waste product, are produced yearly in France. In general, this lignosulfite is not released into rivers, which would be polluted, but is mainly burned to supply steam energy for industry.

4.21 The Extraction Process

Wood processing consists first of eliminating special components such as tannis, resins, and waxes from the wood, which has been stripped of its bark and chipped. Then the lignin and cellulose are extracted according to two basic principles whose choice depends on the eventual use to be made of the cellulose.

A. The first consists of an acid hydrolysis of the polysaccharides in the wood in order to make them soluble in water, or a solution of the cellulose in Schweitzer liquor.

B. The second, used in the paper industry, consists of dissolving the lignin either in alcohol with hydrochloric acid, or in sodium (alkali-lignin) or, as with the method most commonly used in Europe and known as the "bisulfite process", one converts the lignin,
which is insoluble in water, to lignosulfonic acid then to a salt of this acid or water-soluble lignosulfonate. This conversion is effected through the action of sulfur dioxide or, more generally, to avoid the formation of sulfuric acid which darkens the cellulose, with the aid of alkaline bisulfite solutions and solutions of metals of the calcium group \([\text{Ca(HSO}_3\text{)}_2, \text{NaHSO}_3, \text{Mg(HSO}_3\text{)}_2, \text{NH}_4\text{HSO}_3]\) in an autoclave at about 150°C.

This treatment is followed by more or less thorough neutralization with alkaline bases or metals of the calcium group.

One thus obtains a brown or even black lignosulfonate liquor which is used commercially at a concentration of 40 to 60%. This liquor is often heat treated to reduce it to a powder.

Thus, there is a diversity of lignosulfonates: sodium, ammonium, magnesium and, the most common, calcium lignosulfonates, and the solution's pH varies as one passes from one grade to another, and finally, its consistency varies: liquid or a beige to dark brown powder. The liquid, moreover, has slightly different chemical properties, a phenomenon which is most likely due to the heat treatment which is conducive to partial reactions of the lignosulfonate molecules among themselves. The bisulfite treatment gives only a crude product.

4.22 Chemical Composition

A calcium lignosulfonate in powder form will generally have the following average composition:

<table>
<thead>
<tr>
<th>Component</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>total solubles</td>
<td>100%</td>
</tr>
<tr>
<td>dry matter</td>
<td>95%</td>
</tr>
<tr>
<td>moisture</td>
<td>5%</td>
</tr>
</tbody>
</table>

The dry matter is composed of:

- sulfonates lignin salts: 76%
- reducing sugars: 19%
- mineral ash: 4%

The chemistry of lignin is very complex, and there are numerous works on this topic. Many formulas have been developed and suggested over the last twenty years, but all authors seem to agree that lignins are derived from basic units belonging to the \((C_6H_5CCC)\) family, that is to say, they possess a benzene nucléus with a lateral chain of 3 atoms.
According to KLASEN, these units might be linked to coniferyl alcohol:

\[
\text{OCH}_3
\text{HO}--\text{CH = CH} - \text{CH}_2\text{OH}
\]

According to FREUDENBERG, the basic structure might be one of the following:

Thus, the following general formula can be accepted:

\[
\text{OCH}_3
\text{HO}--\text{C} - \text{C} - \text{C} - \text{H}
\]

The molecular mass would be somewhere between 2,000 and 100,000.

The point of fixation for the \( \text{HSO}_3 \) at the time of sulfonation of the lignin by the bisulfite solution is also poorly defined.
According to K. KRATZ and E. RISNYOVSKY, it is attached to the lateral chain, on one of the 3 carbons, for example:

\[
\begin{align*}
&\text{OCH}_3 &\text{SO}_3\text{H} \\
&\text{OH} &\text{C} - \text{C} - \text{C} + \text{Me} \rightarrow \text{HO} &\text{C} - \text{C} - \\
&\text{lignosulphonic acid} &\text{lignosulphonate}
\end{align*}
\]

Whereas, according to BJORKMAN, it is attached, at least partially, in an alpha position on the benzene nucleus.

\[
\begin{align*}
&\text{OCH}_3 &\text{SO}_3\text{H} \\
&\text{OH} &\text{C} - \text{C} - \text{C} + \text{Me} \rightarrow \text{HO} &\text{C} - \text{C} - \\
&\text{lignosulphonic acid} &\text{lignosulphonate}
\end{align*}
\]

\[\text{Me}^{[1]} \text{ being Na}^+, \text{ NH}_4^+, 1/2 \text{Ca}^{++} \text{ or } 1/2 \text{Mg}^{++}\]

4.3 Mechanics of Gel Formation

The action of chromium on the lignosulphonates is at present poorly understood, although the first patent on lignochromiums dates back to 1910. It is assumed that hexavalent chromium in an acid medium or under the action of an acid salt begins by oxidizing the lignosulphonate to form groups of carboxylic acid (SMITH 52-05) and fixes the oxygen atoms to precipitate it in the form of a heavy metal salt. Thus a compact gelatinous mass is formed (lignochromium gel). According to SMITH, a chemical reaction takes place "in situ" between the grout and the ground.

Lignochromium gels perform well in fine sands and silts, but more poorly in coarse sands. SMITH explains this phenomenon in the following way:

After reacting with the lignosulphonates, the chromium still has free valences which fixes the oxygen atoms to particles of ground.

\[\text{[1]}\text{Me} = \text{Metallic ion}\]
In the pores in the ground, the gel swells in the presence of water, while on the surface of the particles a waterproof film forms. This film is a characteristic property of the organo-chromiums which have been used commercially since 1952.

The enormous diversity of the lignochromiums on the market (nature of the cation, state of purification, physical state, concentration, pH) demonstrates the diversity of their uses in laboratories and in industry.

4.4 Composition of the Grout

4.41 Choice of Lignosulfonate

There exist on the world market lignosulfonates of the types Ca$$^{++}$$, Na$$^{+}$$, Mg$$^{++}$$, NH$$^{+}$$; the most commonly used being Ca$$^{++}$$, Na$$^{+}$$, and NH$$^{+}$$.

Allette WESTON and R. A. KENNERLEY (58-15) conducted a comparative study of these three lignosulfonates in a 50% solution.

They deduced that:

(1) Setting time increases as one passes from ammonium lignosulfonate to calcium lignosulfonate and then to sodium lignosulfonate.

(2) Permeability of the salts injected is from 10$$^{-10}$$ m/s to 10$$^{-12}$$ m/s for the ammonium and 10$$^{-9}$$ to 10$$^{-11}$$ m/s for the calcium.

(3) Stability of sodium lignosulfonate is so poor that it cannot be used for grouting; calcium lignosulfonate performs the best (SOLOMON J. REHMAR and NORMAN L. LIVER 62-26; SERLACHIUS 68-09).

REHMAR and LIVER mention that the lignosulfonate should be relieved of part of its reducing sugars (< 8%), allowing a decrease in the proportion of the costly and toxic hexavalent chromium.

4.42 Suggested Formulas

The basic composition of a lignochromium grout is always lignosulfonate plus a hexavalent chromium compound. The nature and amounts of additives used depend on the pH of the sulfite liquor. Since in its oxidation reaction with the lignosulfonate the hexavalent chromium passes from a
Cr$^{6+}$ state to Cr$^{3+}$ only in an acid medium, it is obvious that if no other component is added, the sulfite liquor will be initially acid. Therefore, to the lignosulfate-chromate mixture will be added a definite amount of acid or strong acid salts and a weak base of the following metals: nickel, cobalt, magnesium, iron, chromium, zinc, copper or manganese (SERLACHIUS 68-09).

REHMER and LIVER (62-26) suggest a more complex formula:

- lignosulfonate having less than 8% reducing sugars
- hexavalent chromium salt
- hardening agent of acid or acid salt
- accelerator of copper salt plus a metallic salt (ferric chloride, sodium chloride, calcium chloride or ferric sulfate.

Table 4 summarizes the various compositions mentioned by different authors.

<table>
<thead>
<tr>
<th>Table 4. Lignochrome Grout Basic Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ingredients</td>
</tr>
<tr>
<td>nature of the sulfonate</td>
</tr>
<tr>
<td>sodium bichromate w/ regard to dry weight of lignosulfonate</td>
</tr>
<tr>
<td>Additive 1</td>
</tr>
<tr>
<td>Additive 2</td>
</tr>
<tr>
<td>Dilution: water lignosulfonate</td>
</tr>
</tbody>
</table>
4.43 Industrial Preparation

Since the mixing of the different ingredients on the actual work site demands a great deal of care, it has been suggested that preliminary mixing be done in a plant: REHMAR and LIVER processes (marketed under the name of TERRA-FIRMA) and SERLACHIUS.

In the TERRA-FIRMA process of INTRUSION PREPAKT, which is under the REHMAR and LIVER patent (62-26), one prepares a dry mixture in the plant of the components listed above and then, at the work site, one adds 3 1/2 to 6 parts of water, depending on the setting time desired.

In the SERLACHIUS process, two types of preparation in the plant are suggested. One is identical to the TERRA-FIRMA (dry mixture of all the components). The second is more complex. Two separate solutions are prepared: the first one of sodium dichromate (Na$_2$Cr$_2$O$_7$ • 2H$_2$O), dissolved in its own weight of water and the second one of lignosulfonate, also dissolved in its own weight of water. Both solutions are separately brought to a pH of 7 by addition of sodium hydroxide. These two solutions are then mixed. The pH will rise to between 7.5 and 8.5. This liquor is kept in that state or dried through atomization. Only at the site mixing plant are water and the acid reagent added.

4.5 Characteristics

4.51 Viscosity

The lignochrome grout's initial viscosity of about 2.5 to 4 cP (NEEDLANDS & JAMES 63-06) is comparable to that of silica gels and it increases progressively until it sets (unlike aqueous grouting resins of the resorcinol-formol or the acrylamide type where the change of viscosity is abrupt.) (Fig. 8, C. CARON 63-03).

4.52 Injectability

This low initial viscosity permits injection of lignochrome grouts into fine sands having a d$_{10}$ of between 0.02 and 0.5 mm and a permeability (K) of between 10$^{-3}$ and 10$^{-5}$ m/s, according to C. CARON (65-03), or even a grain size of 0.02 mm and a K of 10$^{-6}$ m/s, according to O. INGLES (69-01), while MITCHELL (70-01) had in mind a much coarser sand: 0.07 to 10 mm.

Measurements of the grout's penetration time in a given sand to a depth of 15 cm have been carried out
Fig. 8. Viscosity-Time Relationship of Lignochrome

CLAUDE CARON (63-03)
mainly by the U.S. Bureau of Reclamation (52-17) and by ALLETTE WESTON and R. A. KENNERLEY (58-15). If a grout takes too long to penetrate, it is deemed uninjectable.

4.53 Setting Time

Setting time varies in accordance with the nature of the lignosulfonate as noted below. It also varies with temperature, as is the case with resins, and obeys ARRHENIUS' law (C. CARON 63-03 and fig. 10, from the BUREC report 52-17). The effect of temperature was the cause of mishaps at the injection site at HAWEA LAKE (G. G. NATUSCH 59-16) and reason for modifications in the grout's formula for the work done at HEART BUTTE Dam (LESLIE P. WHITTE 57-02).

Setting time also varies with the proportions used of the different ingredients:

- dichromate fig 10, according to C. CARON, C. GAILLEDREAU, Y. BELOT (62-21)
- acid fig. 11, BUREC (52-17)
- salt fig. 12, SERLACIUHS (68-09)
- water fig. 13, BUREC (52-17)

For ordinary grouting purposes, setting time will be generally between 10 minutes and 10 hours (C. CARON 63-03), but can take several days (WESTON & KENNERLEY 58-15).

4.54 Strength

Variations in the proportions used of the different components will cause variations in the gel's cohesion and in the strength of the grouted ground. Laboratory measurements of strength have been conducted by CORNELL University, BUREC (52-17) and C. CARON (63-03). While C. CARON spoke of a cohesion of 500 g/cm² and put the strength of the grouted sand at 5 kg/cm² (preserved in airtight conditions), Cornell University's and BUREC's figures were generally higher when obtained in unrealistic dry air conditions.

In order to make test results comparable, some degree of standardization is necessary. The use of standard sands, the method used for making up the test samples, and the conditions in which they are preserved should be standardized. For purposes of comparison with the dry air method BUREC indicates that:
Fig. 9. Effect of Temperature on Setting Time of Chrome-Lignin Gels (Typical Curve)

Modified curves from Cornell University Report

United States Department of the Interior Bureau of Reclamation (52-17)
Formula used:

dissolved mud: 1000 cc
lignosulfite: 1) 210 g/l
2) 230 g/l
antifoaming agent: 5 cc
sodium dichromate: var.

Fig. 10. Setting Time of Lignochrome
Without Perchloride

C CARON, C GAillardreau, Y BELOT (62-21)
Fig. 11. Effect of pH on Setting Time of Lignin Dichromate

Typical diagram of a concentrated mix, pH adjusted with H₂SO₄ or NaOH

Temperature = 65 degrees F

United States Department of the Interior, Bureau of Reclamation (52.17)
Fig. 12. Effect of Salt Concentration on Setting Time of Lignochrome Grout
Fig. 13. Effect of Concentration of Lignin Solution on Setting Time of Lignochrome Grout

UNITED STATES DEPARTMENT OF
THE INTERIOR BUREAU OF
RECLAMATION (52-17)
No. 100 sand (< 0.149 mm) injected without pressure will have, after 7 days, a strength of 7 kg/cm² (96 psi) to 10 kg/cm² (140 psi), depending on the concentration, while a much finer sand ("pan" size sand) injected under 3.5 kg/cm² (50 psi) pressure will have a strength of 51 kg/cm² (735 psi) to 63 kg/cm² (900 psi) if the grout's formula remains unchanged.

4.55 Permeability

Injected into fine grounds with permeabilities of between 10⁻³ and 10⁻⁵ m/s, a lignochrome grout is a very good product for waterproofing. ALLETTE WESTON and R. A. KENNERLEY (58-15) indicate that the grouting of sands within a range of 0.150 and 0.3 mm will give a permeability of 2 x 10⁻¹² m/s with ammonium lignosulfonate, and 3 x 10⁻¹¹ m/s with calcium lignosulfonate.

4.56 Stability

Test samples kept in a water-saturated environment show significant drops in strength over time (fig. 14 BUREC) (52-17). Strength varies according to the conditions under which the sample is preserved. For example:

a. Air curing produces an increase in strength.

b. Preservation in a water-saturated environment produces a strength of 26 kg/cm² (360 psi) on the eighth day, decreasing to 16-21 kg/cm² (230-275 psi) by the end of 15 days.

c. Curing for 20 days in a saturated environment, then air curing for 24 hours produces intermediate strength.

d. Immersed in water after 24 hours of air cure, strength decreases slightly (15 kg/cm²) (220 psi) to 12 kg/cm² (170 psi), according to Cornell University, while BUREC noted no decrease in strength.

e. Dry-wet cycle curing seems to affect the grout since strength is reduced with each cycle.
Fig. 14. Effect of Type of Cure on Compressive Strength of Soil Stabilized with Chrome-Lignin
The lignochromes stand up relatively poorly under prolonged contact with water or, even worse, leaching. However, the lack of published data on this subject and the absence of significant standards rule out any conclusive results.

In tests for severe leaching, C. CARON, C. GAILLE-DREAU and Y. BELLOT (62-21) worked on a 0.1 to 0.3 mm sand injected with lignochrome. The liquid used was a saturated nitrate solution (90Sr). Percolation tests with soft water over a gradient of 50, intended to check the gel's stability by determining losses at 90Sr, indicated losses of about 24% at the end of 12 days. While testing for strength under conditions of external leaching, Allette WESTON and R. A. KENNERLEY (58-15) detected only small losses of chromium (Cr total measured out by titrimetry after 4 and 22 hours) provided the lignochrome is at least 20 days old. In these conditions they consider the grout to be chemically stable.

**4.57 Toxicity**

Rather unpleasant to handle by virtue of their color, the lignochrome grouts, called "monkey's blood" by the engineers who use them (PLAISTED 74-03), have as their principal drawback the toxicity of their components. While O'BRIEN (63-31) speaks even of the toxicity of the ferric chloride which is added in some cases, ATHERTON and GARRETT (59-05) mention incidents of dermatosis contracted by handlers. Numerous authors lay particular stress on the toxicity of hexavalent chromium: CHELLIS (61-05), LESLIE P. WHITE (57-02), NATUSCH (59-16), SERLACHIUΣ (68-09), U.S.B.R. (52-17), SALOMON J. REHMAR and L. LIVER (62-26).

Although hexavalent chromium is reduced to non-toxic trivalent chromium once the grout has polymerized (C. CARON 63-03), lack of care during proportioning or slow chemical reaction can lead to incomplete reduction of hexavalent chromium and cause some contamination of the environment. Several laboratories are trying both to determine those proportions of the different components which release the least hexavalent chromium and to limit its polluting effect.

In general, the rate of hexavalent chromium released by the grout decreases with:
(a) the age of the sample: BUREC tests show that, after leaching, samples which are 7 days old release about 4 times less hexavalent chromium than those which are 24 hours old. ALLETTE WESTON and R. A. KENNERLEY's tests (58-15) show that at the end of a dozen days the gel has practically ceased to release hexavalent chromium.

(b) the pH of the grout or the ground: The addition of sulfuric acid to the mixture stops the gel from releasing hexavalent chromium after 48 hours or limits these releases to very small amounts (BUREC 52-17).

(c) the proportion of chromium in the original mixture: When the proportion of dichromate is reduced by one half (chromium-lignosulfonate ratio = 1/10 instead of 2/10), the amount of chromium 6 released is nil at the end of 24 hours (BUREC 52-17).

Based on this phenomenon, Allette WESTON and R. A. KENNERLEY (58-17) and L. Leslie P. WITTE (57-02) assert that the addition of ferric chloride, to accelerate setting time, reduces the proportion of chromium-lignosulfonate and thus, the grout's toxicity. For the same reason S. J. REHMAR and Norman L. LIVER (62-26) recommend the addition of a large amount of ferric salt or of alkaline lignosulfonates.

All these considerations were taken into account at the time of construction of the HEART BUTTE Dam (Leslie P. WITTE 57-02), situated on a river used to supply drinking water:

After developing a grout material which would release a minimum of hexavalent chromium, the additional precaution was taken (after conclusive laboratory results) of injecting raw lignosulfonate downstream from the injection of lignochromium to intercept the hexavalent chromium. Thus its maximum concentration in the water in the vicinity of the injection was 4 ppm and downstream it was below the 0.05 ppm allowable under United States Public Health Service regulations (57-02).
4.6 Applications

Owing to a lack of experience on the part of the engineers responsible for the formulation of the injection of the grout, some mishaps have been recorded at work sites:

(1) The nature of the lignosulfonate delivered was not the same as that of the samples studied in laboratories. This was true for waterproofing of the buttresses of the dam situated at the outlet of Lake HAWEA, N. Zealand (G.G. NATUSCH 59-16) and for waterproofing of conduit couplings at the HEART BUTTE Dam, N. Dakota (Leslie P. WITTE 57-02).

(2) The temperature of the grout at the time of injection was not the same as that used for laboratory tests (59-16).

(3) The lignochrome was injected immediately following an injection of watersoaked bentonite. The grout would not set. HAWEA LAKE (59-16).

Apart from these few incidents, many waterproofing and consolidation projects have been carried out without problems. Five such jobs include:

(1) Waterproofing of concrete conduit couplings which had been treated initially with bituminous mastic then, unsuccessfully, with a cement grout (HEART BUTTE DAM). The couplings were perfectly watertight at the end of nine months (54-05, 57-01).

(2) Consolidation of the ground under buildings at GREAT CUMBERLAND PLACE in London's West End to permit the construction of underground garages. This work was done by CEMENTATION COMPANY using the "Tube a Manchette" process (61-14).

(3) Waterproofing of a small dam done by INTRUSION PREPAKT (U.S.A.) (53-04).

(4) Ground consolidation for the construction of the Blackwall Tunnel under the Thames using the "Tube a Manchette" process (61-07, 65-05).

(5) Consolidation of sandy terrain at TUDHOE Mill Drift in DURHAM (England) using the "Tube a Manchette" process (59-05, 63-06).
4.7 Rating

Even if lignochrome gels produce only moderate strength similar to semi-hard silica gels, and are toxic before they set (although it is possible to minimize this effect), they have the advantage of low viscosity and easily regulated setting times. They are destined to be developed further since their basic component is in plentiful supply, inexpensive, and is not a petroleum derivative.

<table>
<thead>
<tr>
<th>Criterion</th>
<th>Percentage</th>
<th>for Waterproofing</th>
<th>for Consolidation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>30</td>
<td>6</td>
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</tr>
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</tbody>
</table>
5. CATEGORY A-4: OTHER PLANT DERIVATIVES

5.1 Introduction

The lignochromes are typical examples of grouts whose principal raw material is of vegetable origin. These grouts have been extensively used. Other grouts of the vegetal type have been suggested, but have not been used with the frequency of the lignochrome grouts. The few available references deal with natural resins obtained from fir trees (colophane) or from corncobs (furfural).

5.2 Colophane Type Natural Resins (Rosin and Vinsol)

Colophane is the residual product of the distillation of pitch for purposes of obtaining turpentine. The pitch itself is obtained by incising the trunk of most species of fir trees (pinus palustris in North America). Colophane is composed essentially of abietic acid which, when heated in an alkaline solution, gives the corresponding abietate (Rosin). These abietates are able to disperse large quantities of insoluble abietic acid in colloidal form (Vinsol). For centuries these products have been used to make glues and varnishes.

Thirty years ago natural water-soluble resins, rosin and vinsol, were used for the waterproofing and stabilization of ground surfaces and, more specifically, in road construction (42-04, 43-14, 43-15, 44-01, 44-15, 45-09, 47-01, 48-11).

The best results are achieved with rosinites obtained from ferric and aluminum salts. LOOMIS (39-24) has adapted this method to a two phase grouting process: an aqueous rosinate solution, then an aqueous acid solution are injected into oil wells, leaving the oil-producing strata intact.

For grouting FISCHER (55-07) used a dehydrogenated rosin containing at least 40% dehydroabietic acid and less than 1% abietic acid. It is saponified in solution in water by hydroxides or carbonates of lithium, sodium or potassium and application is always by the two-shot process. A second solution is injected, from 1 to 5% proportionally to the rosin. This will be an aluminum salt or a fatty acid having a chain of 10 to 30 carbon molecules.
After a maximum of 6 hours these two solutions, which are easy to inject, form a solid which resembles grease. The product's hardness can be improved by incorporating synthetic resins into the composition, through the polymerization of $\beta$-pinene or butadiene.

CARPENTER (56-09, 58-12) advocates grouting with an alkali rosin salt (for example, a sodium rosinate) along with a hydrolyzing agent, generally methyl formate or methyl chloracetate. The slow hydrolysis of the ester converts the rosin salt to a water insoluble acid. The hydrolysis can be facilitated by the addition of an oxydizing agent, such as potassium persulfate. Colophane has also been suggested as a modifying agent for phenolic and amino resins.

5.3 Resins Derived From Furfural

Furfural was isolated for the first time in 1832 by DOBREINER. The decomposition of agricultural residues in an acid bath permits the extraction of furfural, a reasonably priced raw material of purely plant origin, with corncobs most frequently used as the basic material. In theory the yield is 24%, but in practice the yield is closer to 12% after unfavorable secondary reactions, which could be avoided by first decoding the xyloses through a biological treatment in an acid medium or by alkaline pre-treatment (76-02).

Unlike the lignosulfites and colophane, which are not clearly defined products, furfural is perfectly defined as a composition, and grouts obtained from it are quite reproducible.

Furfural, whose developed formula is:

\[
\text{C}_5\text{H}_4\text{O}_2
\]

\[
\begin{array}{c}
\text{CHO} \\
\end{array}
\]

has the following physical and chemical characteristics (table 6) (67-11, 76-02)
Table 6. Properties of Furfural*

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>empirical formula</td>
<td>C₅H₄O₂</td>
</tr>
<tr>
<td>molecular weight</td>
<td>96.08</td>
</tr>
<tr>
<td>boiling point (at 760 mm) °C</td>
<td>161.7</td>
</tr>
<tr>
<td>freezing point, °C</td>
<td>-36.5</td>
</tr>
<tr>
<td>density (T/4°C), g/cm³</td>
<td></td>
</tr>
<tr>
<td>at 20°C</td>
<td>1.1598</td>
</tr>
<tr>
<td>at 25°C</td>
<td>1.1545</td>
</tr>
<tr>
<td>solubility in water, at 13°C</td>
<td>9.15%</td>
</tr>
</tbody>
</table>

*(67-11, 76-02)

Furfural is used as an aldehyde to replace formaldehyde in phenolic and amino resins (through combination with a phenol, an amine, such as urea or aniline or even thiourea). Such combinations have been suggested and sometimes used for grouting.

More interesting still are the instances where advantage was taken of the double linkage of the furanic core to obtain a grouting product whose principal ingredient was furfural. This would allow producing a grout material completely free of petrochemicals.

It does not seem that this alternative, however viable in theory, has been thoroughly explored and used. Although not reported in available literature, it has been used in the Soviet Union for consolidation grouting for collieries, in non-calcareous terrain. The YOUNG patent (65-21) describes a two-shot injection into sand: first a mixture of a prepolymer of furfurylic alcohol dissolved in the monomer, then the acid catalyst.

It seems that if the basic pattern of these furfural derivatives can be obtained in an alkaline medium, the final polymerization must take place in an acid medium. This factor considerably limits the possible usefulness of these products for grouting, although the possibility of basic catalysis has been pointed out.
In spite of these reservations, two furanic derivatives might be usable for soil grouting, furfurylidenacetone and furfurylic alcohol.

a) **furfurylidenacetone**

From the reaction of 3 molecules of furfural on 2 molecules of acetone, a mixture of monofurfurylidenacetone and difurfurylidenacetone results as follows:

\[
\begin{align*}
3 \quad \text{CHO} + 2 \quad \text{CH}_3 - \text{C} - \text{CH}_3 & \quad \rightarrow \\
\text{CH} = \text{CH} - \text{C} - \text{CH}_3 + \quad \text{CH} = \text{CH} - \text{C} - \text{CH} = \text{CH} & \\
\end{align*}
\]

which then polymerizes while subject to rising temperature, or passing into an acid medium (67-11, 70-18, 70-19).

In the field of Public Works, these resins have been the subject of some research for their possible uses as binder in special concretes (70-18; 70-19). In principle, a furfural-acetone prepolymer is used, to which a hardener is added (sulfonic benzene acid).

b) **furfuryl alcohol**

Through hydrogenation, furfural results in furfuryl alcohol, which has remarkable reactive properties. This product whose developed formula is:

\[
\text{CH}_2\text{OH}
\]

has the following physical and chemical characteristics (table 7)

<table>
<thead>
<tr>
<th>Table 7. Properties of Furfuryl Alcohol (67-11)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>empirical formula</strong></td>
</tr>
<tr>
<td>$\text{C}_5\text{H}_6\text{O}_2$</td>
</tr>
<tr>
<td><strong>molecular weight</strong></td>
</tr>
<tr>
<td>98.1</td>
</tr>
<tr>
<td><strong>boiling point (760 mm), °C</strong></td>
</tr>
<tr>
<td>170</td>
</tr>
<tr>
<td><strong>refractive index, $n^\circ_{20}$</strong></td>
</tr>
<tr>
<td>1.4868</td>
</tr>
<tr>
<td><strong>density, 20/4°C</strong></td>
</tr>
<tr>
<td>1.285</td>
</tr>
</tbody>
</table>

67
In an acid medium, this alcohol can polymerize to the point of forming a hard mass as seen in the diagram below (67-11):

\[
\begin{array}{c}
\text{\includegraphics[width=\textwidth]{diagram.png}}
\end{array}
\]

Apparently the direct polymerization of monomeric furfurylic alcohol has never been contemplated or used. Linear prepolymers or monomeric-polymeric mixtures are preferred. The prepolymerization of the furfurylic alcohol takes place under heat in a generally acid medium (mineral or organic acid or salts which have been aminated or amidated with a strong acid). At the moment when the condensed water is eliminated, the medium is made once again neutral or basic.

Depending on the procedure used (temperature, pH), one arrives at a rather condensed substance and, consequently, at a rather viscous prepolymer ranging from less than one cP to several hundred cP. For grouting purposes, one must choose a method of preparing the prepolymer which will give a substance with low viscosity. To lower viscosity, dissolving the prepolymer in the monomer is a perfectly valid procedure (monomeric furfurylic alcohol has a viscosity of 4.62 cP at 25°C). It is also possible to dilute it with water.

In addition to the homopolymerization of furfurylic alcohol (the hydroxyl group of the furfurylic alcohol reacts on an alpha hydrogen of another alcohol molecule (54-19, 62-33, 64-22), this alcohol could be combined with furfural, formaldehyde or an aliphatic alcohol (47-15, 50-21, 51-13).

Even if the reaction can be initiated in some cases in an alkaline medium, it is virtually certain that the final stage can only be obtained in an acid medium. It seems, however, that it is possible to work with a slightly acid medium, but condensation at a pH higher than that bringing on the attack of carbonates has not yet been verified.
Finally, reviewing other types of uses (adhesives, casting molds, carbon and graphite binders), the use of furfuryl alcohol in conjunction with urea-formaldehydes, phenol-formaldehydes, and others, is possible.

5.4 Rating

It is virtually impossible to assign ratings to products whose possible applications in grouting have been studied so little and have been so little used for that purpose. Performance and long-term durability are practically unknown for this category. In the absence of precise ratings, a list of foreseeable advantages of Category A-4 products is included.

Of some 20 categories of grouts, only two (A-3 and A-4) are of plant origin. Thus, if petrochemical derivatives become unavailable and even mineral derivatives are in time exhausted, there will remain an inexhaustible source in agriculture. Of these two vegetal categories we have already seen the advantages and drawbacks of Category A-3, lignosulfite derivatives. Their principle shortcoming is that the polymerization of this chain is possible only with sodium dichromate, a very toxic substance. There is no inconvenience of this nature for Category A-4, furfural derivatives. This category includes two main products: colophane derivatives, from fir trees, and furfural derivatives, from corncobs.

Colophane derivatives, Rosin and Vinsol, have been under study for twenty years and have been used tentatively a few times. This alternative is not very promising because it would lead, at best, to a waterproofing grout which would have to compete with the silicate-based soft gels, among others, which clearly perform better and cost less.

On the other hand, the furfural derivatives could lead to high consolidation grouts, a field in which competing grouts would be petrochemical derivative products. Thus, the furanic alternatives are promising, since the possibilities for supply are nearly limitless. For example, a rapid survey in France showed that the present productive capacity of furfural is 10,000 tons and could be brought up to 240,000 tons, using corncobs alone as a source, and that it would be perfectly feasible to use other sources of supply such as bagasse, sunflower seed husks, industrial leaf residues, straw, paper mill effluents and even garbage. France's capacity would be 4,000,000 tons per year, or 400 times its present capacity.
Although the yield is less favorable with these new potential sources of supply than that obtained from corncobs, it is good enough to justify industrial processing (table 8).

<table>
<thead>
<tr>
<th>Products</th>
<th>Present yield</th>
<th>Tonnages</th>
<th>Potential of furfural, tons</th>
</tr>
</thead>
<tbody>
<tr>
<td>straw</td>
<td>6%</td>
<td>30,000,000</td>
<td>1,800,000</td>
</tr>
<tr>
<td>corncobs</td>
<td>12%</td>
<td>2,000,000</td>
<td>240,000</td>
</tr>
<tr>
<td>rice husks</td>
<td>6%</td>
<td>80,000</td>
<td>4,800</td>
</tr>
<tr>
<td>olive cake</td>
<td>7%</td>
<td>3,500</td>
<td>245</td>
</tr>
<tr>
<td>sunflower seed husks</td>
<td>10%</td>
<td>75,000</td>
<td>7,500</td>
</tr>
<tr>
<td>colza husks</td>
<td>12%</td>
<td>105,600</td>
<td>13,300</td>
</tr>
<tr>
<td>paper mill effluents</td>
<td>10%</td>
<td>5,167,470</td>
<td>516,747</td>
</tr>
<tr>
<td>garbage</td>
<td>3%</td>
<td>12,000,000</td>
<td>360,000</td>
</tr>
<tr>
<td>Provence reeds</td>
<td>9%</td>
<td>400,000</td>
<td>36,000</td>
</tr>
<tr>
<td>sawdust and slash</td>
<td>6%</td>
<td>7,124,700</td>
<td>427,482</td>
</tr>
</tbody>
</table>
6. CATEGORY A-5: POLYACRYLAMIDES

6.1 Introduction

The processing of primary products necessary to obtain polyacrylamide resins dates back to the end of the last century; however, the use of these products for the production of synthetic resins is much more recent. These resins were the first to lead to products used specifically for soil grouting. Of these products, the oldest and best known is the resin developed by American Cyanamid and marketed under the name AM-9.

It was the success of this grout which led to research into other resins such as the phenoplasts, and spurred the development of that range of resins which can polymerize in aqueous solutions and which are successfully used at present for grouting fine sand.

The primary product used to obtain a polyacrylamide resin is a monomeric acrylamide which, as its name implies, is an ethylenic amide. Such a compound can thus react either through its double bond or through its amide function. The double bond allows the radical in the monomer to polymerize along the general pattern of vinyl compounds, while the amide function allows condensation with aldehydes. In addition, acrylamide can replace urea in aminoplasts.

In order to be familiar with the reaction mechanisms and the general properties, as well as possible applications of polyacrylamides, it would be useful to refer to the work of D.C. MAC WILLIAMS "Acrylamide and other Alpha, Beta Unsaturated Amides - Functional Monomers, Vol. 1" Pub. M. Dekker 1974. The polymerization of monomeric acrylamide can take place in an aqueous solution; it can be initiated by heating, by ultrasonic waves, by gamma rays, and for the case which concerns us here, by a catalytic method of the redox type (peroxide).

The homopolymerization of the acrylamide leads to linear polymers of variable molecular weight which are perfectly soluble in water. To obtain an insoluble polymer, it is necessary to combine it with a reticulating agent.

Although chemistry offers a whole array of non-saturated amides, only acrylamide and methacrylamide are used industrially to obtain polymers. N isopropyl acrylamide and N methylolacrylamide have also been suggested.
Reticulation is generally obtained through the inclusion of small amounts of a dimer such as methylenebis-acrylamide which allows the establishment of a bridge between two linear chains of polymers. However, other water-soluble divinyl compounds may be used. Reticulation of the polymer could also be obtained through the reaction of an aldehyde on the amide function. For this purpose, the principal products recommended have been formaldehyde and glyoxal.

The degree of reticulation, which will determine more of the properties of the polymer obtained, can be regulated according to the amount of reticulation agent included in the mixture. It should be noted that when an aldehyde is used as a reticulant, condensation becomes preponderant when the proportion of aldehyde approaches stoichiometric quantities and the product obtained will have properties comparable to urea formaldehyde resins as defined in the section covering aminoplasts (68-10).

Polymerization at ambient temperature is brought on through the action of a redox-type catalyst which includes an initiator or primer of peroxide or persalt type (most often a persulfate) and an accelerator or activator, which is most often of the dimethyl- or diethylaminopropionitrile type. Other compounds of the same type have also been suggested (59-14). Currently, ammonium persulfate is designated as AP; dimethylaminopropionitrile is DMAPN, and diethylaminopropionitrile is DEAPN.

The time necessary for the reaction is determined by the respective proportions of DMAPN or DEAPN and AP. To gain even more flexibility in the adjustment of the setting time, it is possible to include a small amount of a reaction inhibitor, most often potassium ferricyanide, K₃Fe(CN)₆. Other acrylic compounds, such as calcium acrylate (53.03, 53-07, 53-11, 61-05, 62-17), have also been suggested. These products can be used alone or in combination with an acrylamide (62-25, 68-07). Acrylic acid polymers can also be used in some cases (64-17). J. A. JANSEN and C. R. SUPPLEE (52-08) made a very thorough study of calcium acrylate and methylacrylamide grouts. This study includes both the chemistry of the grouts and the behavior of grounds which have been treated with them.

With regard to polymers obtained from acrylamide and its derivatives, most of the studies and publications on this topic have been the work of AMERICAN CYANAMID CO. and are concerned with the commercial product AM-9 whose name is derived from the fact that it contains 90% monomeric
acrylamide (A.9), and 10% methylenebisacrylamide (M). To become familiar with the general properties of this product, one can consult the document published by American Cyanamid Co.: AM-9, CHEMICAL GROUT (99-03, 99-04) as well as documents published by RHONE-PROGIL (99-13) and by the SUMITOMO CHEMICAL CO., LTD. (99-14).

6.2 Resins Used in Ground Treatment

Acrylic resins in general and polyacrylamide in particular have found three uses in the field of civil engineering:

1) the treatment of ground surfaces;
2) ground treatment in conjunction with oil drilling;
3) grouting by injection.

These different applications generally require different products. For surface soil stabilization, acrylate-type products have been recommended most often (55-09, 53-07, 52-03, 51-03, 50-13, 50-09). Solutions and emulsions of triazine-type vinyl compounds have also been mentioned (58-11). It should be noted that this sort of treatment is applied most often to clayey soils, which is why calcium acrylate is used, since it would most likely fix itself through permutation to the sodic clay particles (55-09). The principal objective is to make the ground impervious to water.

Acrylamide-type compounds have also been suggested for stabilization. Some experts advocate the use of viscous linear polymers (polyacrylamide), which can be reticulated with glyoxal and thus immobilized (74-02). Products analogous to those used in ground grouting have also been advocated.

For grouting in conjunction with oil drilling, the number of processes is rather limited. The use of a slurry has been suggested: acrylamide resin plus fine sand or filler (65-18), as well as the injection of a dispersion of resin in a hydrocarbon. In this case, the precipitation or coagulation of the resin is brought about through the injection of an anionic solution (54-10). This product, too, is viscous and can even contain particles in suspension.
For soil grouting the primary product has been acrylamide, combined with a reticulant: NN'-methylenebis-acrylamide (5 to 15%), glyoxal, formaldehyde. Many other compounds have been suggested (57-19, 67-08), but since these products have not been used in any notable applications, they are not included here.

As reaction activators, nitrilotrispropionitrile (59-14), DMAPN and DEAPN have been suggested. As a catalyst one can use a water-soluble persalt, a per-acid or a peroxide: persulfuric, perboric, perchloric or permanganic acid or their ammonium, potassium, sodium or hydrogen peroxide salts (57-19). The addition of acrylate has also been suggested to allow reaction with the ground (68-07).

These grouts have been widely used for waterproofing concrete structures, especially in Europe where these products must be imported and are quite costly and have therefore been supplanted by phenoplasts for soil grouting applications. The formulas of the grouts used on concrete are generally identical to those used in ground grouting, although some special products have been suggested (64-17).

6.3 General Properties of Acrylamide Grouts

For the most part, acrylamide-base grouts are commercial products which already contain the necessary amounts of acrylamide and its reticulant. These products are marketed under the following brand names:

AM-9: AMERICAN CYANAMID CO.
Rocagil: RHONE PROGIL
Sumisoi: SUMITOMO CHEMICAL CO.

To learn the properties of these different grouts it would be useful to consult the technical data published by these suppliers, making allowance for the advertising nature of such texts.

These products are marketed either in the form of a powder (AM-9, SUMISOIL), or in the form of a concentrated solution (ROCAGIL). At the time of actual use, one must add the catalyst and accelerator to the commercial product (monomeric acrylamide plus reticulant) and dilute with water. The general properties of the grout will depend on the respective proportions of the various components.
6.31 Viscosity

Initial viscosity of the grout depends essentially on the proportion of monomer used. It varies between 1 and 8 centipoises for a dry matter content ranging from 5 to 44%. The traditional 10% solution will have a viscosity of about 1.2 cP at 20°C. Viscosity remains practically unchanged over the whole period of incubation up to the point where the grout sets abruptly (fig. 15).

6.32 Setting Time

All other factors being equal, setting time will be affected by the formula's dry matter content. The higher this concentration, the shorter will be the setting time. The sharpest variations have been observed within the range used most frequently, 5 to 15%.

For a given concentration, setting time will be determined by the proportions of catalyst and activator used. Although these compounds are not always specified in the manufacturer's documentation, it seems that ammonium persulfate (AP) and dimethyl- or diethylaminopropionitrile (DMAPN or DEAPN) are always the products used. The amount of AP can vary from 3 to 0.25% by volume of the grout as a whole, while the DMAPN or DEAPN content will range from 0.1 to 3%.

According to authors on this subject, setting time can be changed either by keeping the AP content constant and varying the amount of DMAPN or DEAPN or by using a constant amount of activator and varying the amount of AP. Such variations in proportions allow little latitude in the setting time at a given temperature. At a temperature of 20°C, the setting time of a 10% solution can be varied between 1 minute and 25 minutes approximately. Thus the grout is workable for only a relatively brief time, especially if the work is not carried out on a continuous basis.

Longer setting times can be easily obtained by the inclusion in the grout of a polymerization inhibitor (60-13). Generally, potassium ferricyanide is used at 0.002 to 0.35% of the grout as a whole. Thus the setting time can be considerably increased and regulated to extend to over one hour. Very long setting times (several hours to several days) seem to be very difficult to obtain without affecting the final properties of the resin.
Fig. 15. Viscosity-Time Relationship of Calcium Lignosulfite, Sodium Lignosulfite and AM-9

CARON (63-03)
Setting time is considerably influenced by temperature, the speed of the reaction following Arrhenius' law quite closely. To simplify a bit, it could be said that the setting time is tripled each time the temperature is lowered by 10°C. An example of the relationship between setting time and temperature is shown in fig. 16.

Setting time can be affected by the pH of the medium, the pH of the water in the solution or the pH of the water in the ground. As a general rule, setting time increases and can become unpredictable in an acid medium while it decreases sharply in an alkaline medium. An excessively high pH can also bring about partial saponification of the monomer and thus harm the grout's final performance. To avoid these problems, one can buffer the grout with a mixture of disodium and trisodium phosphate at a pH of about 9.2 to 9.6.

Some salts, like certain metals (iron, copper), can modify the setting time as can ultra-violet rays, which are powerful polymerization initiators.

It should be noted that, like all aqueous grouts, these grouts are sensitive to frost, but are compatible with currently used antifreezes. This property allows them to be worked at temperatures below 0°C for exceptional cases. In short, these somewhat reticulated acrylamide base products allow the user to easily regulate their setting times over a wide range of temperatures.

6.33 Mechanical Properties

These grouts have been the subject of some tests of unconfined compressive strength carried out on pure gel. These tests show that the resin alone has low mechanical strength (a maximum of a few g/cm²) but great flexibility (20 to 40%) with purely elastic behavior. In any given dilution, the mechanical properties will be affected by the degree of reticulation and the proportion of catalyst used (essentially by the ammonium persulfate).

<table>
<thead>
<tr>
<th>degree of reticulation</th>
<th>strength</th>
<th>flexibility</th>
<th>elasticity</th>
<th>modulus</th>
</tr>
</thead>
<tbody>
<tr>
<td>proportion of AP</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Fig. 16. Correction of Setting Time According to Grout Mix Temperature
Given the weak mechanical properties of the grout alone, one could expect mediocre strength in the sand treated. But the excellent gluing power of this material causes the grouted ground to acquire notable strength, even when the monomer content is low. The coefficient of ground strength in pure grout is about 50.

A study of the mechanical properties of one of these grouts (AM-9) compared with those of other types of grouts is set forth in a document (72-04) which has been a subject of discussions (73-03, 74-07). Laboratory tests have also allowed a determination of the mechanical behavior of AM-9 in the ground treated (58-01) as well as the behavior of acrylates in the treatment of ground surfaces (53-03). It should be noted, however, that these grouts will never give high strengths. Grouts with the right setting time to be really workable will never give results exceeding a dozen bars in the treated ground. In most cases, these strengths attain between 4 and 10 bars.

It has been mentioned that strengths are affected by the degree of reticulation and the proportion of dry matter used. However, the effect of the degree of reticulation becomes limited as the proportion of dry matter is increased. One can thus consider that the 10% reticulant content in AM-9 attains and even exceeds the optimum dose.

As the proportion of basic resin used increases, so the grout's strength increases. However, the cost of a grout using large proportions of resin is quite high, so that the proportion of resin used is usually 10%.

6.34 Permeability after Injection

The impossibility of obtaining strong mechanical properties has often caused the acrylamide grouts to be used for waterproofing. Consequently, the manufacturers have begun defining an intrinsic permeability in the treated ground, the overall permeability being obviously linked to the quality of the injection. The tendency is to assert that AM-9 is completely impermeable.

In fact, sand treated with AM-9 is not totally impermeable, nor is the pure grout. There is no real permeability in the sense intended by Darcy, for the phenomena causing water to percolate are very complex (osmosis). For the sake of consistency and simplification, we will say that there is some permeability. Measurements have put $K$ at about $10^{-10}$ m/s or even $10^{-12}$ m/s. Since this permeability is comparable to that found in clays, it is reasonable, in view of the degree of watertightness desired, to consider such a grout impermeable.
6.35 Durability

Recent tests have shown the performance of these grouts to be excellent under conditions of slow, gradual stress: gradual breaking-in, pressure, slackening (76-01).

Provided that the grout contains enough reticulant, polymerization leads to a stable, practically insoluble product whose durability is thus guaranteed. It must be remembered, however, that a fraction of these grouts can remain hydrolyzable. In some very alkaline mediums, or if the degree of reticulation is insufficient, part of the grout, even if it is polymerized, can hydrolyze and once again become soluble in water, thus disturbing the properties of the treated ground.

6.36 Toxicity

Studies undertaken by AMERICAN CYANAMID have shown that even if the primary products used are highly toxic and require certain precautions at the time of use, the polymer obtained loses all of this toxic character. Also, any products which might leach out of the grout (salts, hydrolyzed matter) are likewise harmless, provided that the formula used was successful in bringing about nearly complete polymerization. It should be noted that free acrylamide is rapidly absorbed by certain micro-organisms, which also limits long-term toxicity.

6.37 Behavior of Polymerized Grout in Presence of Water

AM-9 grout has a remarkable property: after polymerization it forms a nearly perfect colloidal gel. Once immersed, the gel can absorb even more water than was used in its preparation and this quantity further increases if there is little reticulation. In the most extreme case, the grout could thus swell indefinitely and practically dissolve. Conversely, if the degree of reticulation is too high, the grout will contract and expel water as it sets. This behavioral characteristic explains how the hardened grout, after losing water through drying, can reabsorb water if it is moistened. Such phenomena in treated ground occur slowly, and usually do not have to be taken into account. On the other hand, this characteristic explains why these resins have been used so successfully for waterproofing concrete structures.
6.4 Acrylamide Base Grouts

Acrylamide grouts can be modified by many different compounds. For economy one can add substances (sand, filler) used in cement, but the resulting products fall outside the scope of this study.

On the other hand, they can be combined with many other grouts: silica gels, colloidal suspensions, bituminous emulsions and others. These grouts will be analyzed elsewhere in this study.

6.5 Preparation and Injection Technology

Since chemical manufacturers have developed these grouts, in an effort which parallels their marketing programs, they have endeavored to identify the technologies which should be used in the preparation and injection of these products. When they first appeared, these grouts constituted a revolution both for their properties of injectability and for their setting characteristics. Consequently, many authors sought to develop techniques appropriate to the properties and applications of the grouts. Three methods can be used to prepare the grout:

1) the continuous method
2) the semi-continuous method
3) the discontinuous, or interrupted, method

Fig. 17 shows diagrams of these methods.

A general description of the various techniques as applied to different purposes (surface, injection into the ground, oil drilling) has been given by JOHN P. GNAEDINGER (55-01); the procedures suitable for injection have been described by R. H. KAROL (60-06).

The traditional discontinuous method of preparation is unquestioningly accepted and used the most frequently. The other two have been the subject of special publications: (63-18, 99-15) for the continuous method and (62-10) for the semi-continuous method. The general principles of grouting are also defined (54-05, 57-02, 72-03, 73-01) as well as the grout's movement through the ground (68-02, 61-13, 57-01).

6.6 Applications

As has already been indicated, there are three types of applications for acrylamide resins:
a) discontinuous preparation

b) semi-continuous preparation

c) continuous preparation

RHONE-PROGIL (99-13)

Fig. 17. Grout Mix Preparation Methods
1) treatment of ground surfaces
2) oil-well drilling
3) ground grouting and, by extension, concrete and masonry structures

There is a great deal of literature dealing with applications of these products, even where the applications have been few in number, mainly due to the revolutionary nature of the grouts in terms of injectability and setting characteristics.

Acrylate compounds (51-06, 57-05, 60-04) have been used most often for the treatment of ground surfaces. For injection into soils, acrylates have been very little used although they have been recommended in a general manner (62-17). It is therefore the acrylamide-base grouts which are used most frequently for grouting.

Although the merits of these grouts have been universally recognized (61-08, 63-03, 63-37, 65-01, 67-02, 67-04, 69-03, 69-06, 74-09, 62-04), their rather high price makes them generally noncompetitive with silica gels and phenoplast resins, which are more economical and offer a broader range of performances. As a result, applications vary widely from one country to another. This type of grout has not been used very extensively in Europe, although there are a few references to its use in Great Britain, notably for the construction tunnels and wells (63-06, 63-05, 65-05), and in France (99-15). Although a major consumer of these products over the last decade, Japan offers little information on uses made of them, aside from advertising material put out by manufacturers and contractors.

Most of the data concerning applications comes from North America. In addition to the general articles noting possible uses for these resins in injections (57-01, 61-05, 74-09, 63-31, 54-05, 57-02, 61-04), one should take special notice of:

- Applications in mines for support structures (64-04) or to stop seepage (60-03, 61-09). A comparative study with various other grouts (silica gels, lignochromes) was carried out for AM-9 (62-11). It seems that these techniques have been primarily developed in Canada.

- In the field of civil engineering, these grouts have been used to consolidate foundation soils for various structures (69-01, 70-01, 61-11, 59-03, 55-10, 54-01) and for dams (66-02, 63-27, 62-23, 63-18, 65-15).
Ground waterproofing and consolidation for the construction of tunnels, mine galleries and wells (62-10, 62-08, 62-09, 64-06, 59-12, 59-07, 63-32, 62-06, 62-03, 64-01, 64-03, 64-07, 61-12, 63-27).

Finally, acrylamides have also been used to allow sampling of powdery soil through core-drilling (62-14) and to stabilize quicksand (60-02).

6.7 Rating

The polyacrylamide resins constitute a range of grouts with remarkable properties: low viscosity which remains practically constant until the point of set, setting times which can easily be regulated over a wide range. These characteristics make such grouts very easy to use.

These grouts, however, do not confer strong mechanical properties on the ground treated, and the toxicity of the primary products used and the risk of contamination resulting from a poorly formulated grout necessitate special precautions. Commercial products which are ready for use allow small users to avoid risks, but on work sites where many tons of these products must be used, it is more economical to start with primary products and formulate the grout at a mixing plant.

The primary products used in the manufacture of these grouts are petrochemical derivatives, which is a handicap within the scope of this study, especially since these grouts must contain at least a minimum percentage of them. The usual proportion of petrochemical derivatives is about 10%, or 100 kg of primary product for each m³ of grout.

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|                    |            | 4.80            | 4.15             |

Table 9. Rating Chart, Polyacrylamides
Basic research on the condensation of phenols in combination with aldehydes dates back to the last century. But BACKELAND, in 1909, was the first to obtain patents on the industrial preparation of phenoplasts.

The concept of possible applications for these substances in the field of civil engineering doubtless stems from the considerable development they underwent for use as glues and it is in the numerous reference works on these glues that are found the antecedents of the products which are of interest to us today, for example, Pt. SMITH (Synthetic Adhesives 1 1943).

It was not really until the Second World War, however, that the use of these resins was contemplated for grouting, principally in the oil industry, and as a substitute for asphalt in the treatment of ground surfaces, and it was not until the 1960's that resins of this type were used for grouting in underground and foundation construction.

Phenoplast resins are polycondensates obtained through the reaction of phenol on an aldehyde. These resins set under heat and, in their final form, assume a three-dimensional structure which is insoluble and non-fusible. This structure can be outlined as follows:
The conversion from the initial state to the final insoluble, non-fusible product can take place in many different ways. In general, polycondensation can be achieved by one-step or two-step processes (the creation of a precondensate). The reaction can take place in either an acid or alkaline medium. Many different catalysts have been suggested, but there are even other possibilities:

**acid catalysts**: Hydrochloric acid, sulphuric, phosphoric, boric acid; organic acids: acetic, lactic, formic, oxalic, tartric, citric acid, etc.

**basic catalysts**: sodium hydroxide, potassium hydroxide, ammonia, milk of lime, barium hydroxide, aniline, hydrazine, 1-cyanoquainidine, p-aminophenol, xylidine, toluidine, benzidine, diphenylamine, piperidine, dimethylamine, paraminodimethylaniline, etc.

**salts**: sodium carbonate, zinc chloride, trisodium phosphate, sodium phtalate, ammonium bicarbonate, calcium chloride, ammonium chloride, stannic chloride, calcium bromide, sodium salicylate, sodium thiocyanate soaps, such as stearates, palmitates, oleates, resinates, etc.

A careful choice of catalyst and the proportion used can affect considerably the speed of the reaction and also the properties of the final product.

At ambient temperature, a basic catalyst generally will not work, but an acid medium is rarely suitable for grouting: if the soil is at all chalky, the catalyst will react immediately with the calcareous particles and thus lose all effectiveness.

In 1955, in a publication outlining the various organic products which could be used in ground treatment, T. A. MARKUS stipulated that phenol-formaldehyde resins could not successfully be used for this purpose because they could not be made to polymerize at low temperatures and at low pressures (55-09).
Research on wood glues, in particular that conducted by G. F. LITTLE and K. W. PEPPER (Chemical Research Laboratory, Teddington, Middlesex), has shown that the pH of the medium has a strong effect on the speed of the reaction, but also that, with most phenols, the substance would set at normal temperatures (20°C) only in an acid medium. Only certain polyphenols, of which resorcinol is one, can react in an alkaline medium.

In a broad sense, polycondensation of different phenol-aldehyde combinations in an alkaline medium can be obtained only by raising the temperature of that medium. This is what happens, thanks to geothermal temperatures, in the case of grouting for purposes of oil-well drilling. In conjunction with this, there is a multitude of patents, primarily American, claiming that it is possible to treat subterranean formations with phenolic resins. For these purposes, all sorts of phenols and aldehydes are recommended.

Most authors specify that polycondensation is obtained through the elevation of temperature, since most of these injections take place deep in the earth. Some authors are content to specify only that solidification of the resin takes place at the temperature of the site injected. Further details on these points are available in the following references: 36-07, 42-08, 43-02, 44-09, 44-18, 47-11, 48-20, 49-16, 49-17, 40-05, 50-16, 50-17, 52-14, 54-11, 55-11, 55-13, and 57-20. This list is obviously not exhaustive, and some of these references might be considered rather irrelevant.

In a certain number of cases, the use of highly reactive phenols in combination with ordinary phenols has been recommended, permitting final condensation at relatively low temperatures. In all these cases, a precondensation of the phenol-aldehyde combination is brought about until the substance reaches an intermediate stage where the resin is still slightly soluble in water or can be put into suspension (in some cases an oil-soluble precondensate is used). The product injected is thus still viscous (in principle, some hundreds of centipoises).

These two conditions, that the product used be viscous, and that it be injected deep into the earth where the temperature is higher, rule out the use of the products advocated here for the grouting of fine soils near the surface of the ground.
However, in some cases it has been specified that the rise in temperature necessary for condensation could be obtained by applying heat externally. This approach is obviously theoretically possible for grouting, but no actual cases of using the procedure have been found. It is likely that technical and, especially economic considerations, would make this procedure unfeasible.

Military needs during the last world war generated extensive research on the stabilization of ground surfaces. The objective of this research was to find products which could be substituted for asphalt and used in much smaller quantities, for the purpose of stabilizing clayey soils by plugging them with small quantities of resin. The products and procedures used do not meet the definition of grouts, although in some cases there are formulations which could be used, in principle at least, as grouts (72-10, 52-09). The name of WINTERKORN, well known in the field of grouting, occurs in connection with this work. G. E. MURAY (52-03) and MARKUS (55-09) have reviewed the principal products used for stabilization.

7.2 Products Useable in Grouting

The procedures given above for the condensation of phenol with an aldehyde do not produce the conditions necessary for soil grouting, since the substance must be heated to keep the precondensate from being too viscous, or an acid catalyst must be used which is precluded by the fact that normal soil is always at least slight alkaline. This is why this approach for grouts has not been pursued, with the exception of an example cited for Roumania (73-03) where a formol-formaldehyde precondensate, catalyzed by an acid and whose viscosity was lowered through dilution with acetone, was used.

It was not until the 1960's, following the CARON patent (59-17), and the applications of that technique abroad (63-37, 67-07), that phenoplasts could be used for grouting. This process involves a substance highly reactive in unheated conditions, even in a dilute medium of the resorcinol-formaldehyde type catalyzed in a basic medium. The level of viscosity at the time of preparation ranges from 1.5 to 2.5 cP depending on diluteness. By varying the diluteness it is possible to obtain grouts suitable for consolidation (up to 60 some bars) or for waterproofing.
These basic advantages over other grouts in existence at that time (silica gels with high concentrations of silica and therefore viscous, and acrylamides, which would not produce strong consolidation) led rapidly to important applications of this new process.

This new market caught the attention of chemical concerns. Without always realizing that the outstanding feature of these grouts was their low viscosity, these chemical concerns researched and marketed a certain number of products based on highly reactive phenols, in one form or another, which were all somewhat viscous. The best known, RHONE-PROGIL in France and BORDEN in Great Britain, marketed two products whose nature and properties were rather similar:

ROCAGIL (PROGIL Co., France) This product is made up of a solution of partially sulfonated polyphenols of natural origin (tannin) which reacts with formaldehyde in an alkaline medium. The properties of this grout are similar to those obtained with a resorcin-formaldehyde grout except that the viscosity of ROCAGIL is considerably higher: from 5 to 10 cP, depending on the degree of concentration (71-04, 72-03).

GEOSEAL (BORDEN, Great Britain) This product is also ready mixed and needs only to be dissolved in the desired amount of water. According to the terms of the BORDEN patent (66-08), it includes a mixture of tannins and mimosa extract and occasionally a phenolic precondensate, which polymerizes in the presence of formaldehyde or paraformaldehyde in an alkaline medium. The substance's viscosity, which ranges initially from 2 to 12 cP, depending on its concentration, alters considerably before the set. The mechanical properties obtained are weaker than those obtained with the resins described previously.

Another product, TERRANIER (RAYONIER Inc., U.S.A.) should also be mentioned here, since it contains in part a polyphenol base. There is some ambiguity about the reaction mechanism of this product which, in some ways, could be grouped with the lignochromes since the properties of the final product are rather close to those of lignosulfite-base grouts.
Other than commercial products, which are generally complex and poorly defined, phenoplast grouts always contain resorcin or by-products containing large amounts of resorcin (KARGUINE 70-20 and DEMINE 71-07, 73-07). Since resorcin is not an industrial chemical, but a pharmaceutical product, much research has been conducted to find a way to partially replace it by different phenols in precise proportions. All sorts of different phenols have been tried (ordinary phenol, cresols, xylenols, 65-23).

Another polyphenol has also been proposed: phloroglucinol. Since this is a triphenol, it is even more reactive than resorcinol. But as only small quantities of it are produced industrially, at an extremely high price, it remains primarily an object of scientific curiosity which has never progressed beyond the laboratory.

The aldehyde used is practically always formaldehyde in a 30 to 40% solution in water. Paraformaldehyde can be used as a substitute since it is cheaper to transport, but this product is somewhat harder to use since it does not dissolve readily in water. Furfural has also been recommended.

7.3 General Properties Of Phenoplast Grouts

In the field of grouting, it is not the resin's chemical properties which are critical, but its characteristic properties with respect to the different qualitative standards used to judge grouts: rheological behavior before setting, setting time and mechanical strength of treated ground. To these can be added properties involving the environment: durability with regard to ion stress and toxicity. It is therefore of great theoretical interest to examine the behavior of the resorcinol-formaldehyde basic resin, since the mechanical process of polycondensation of these two materials in combination adheres to strict rules. Other products which have been suggested can be analyzed similarly. A typical grout would be composed of resorcinol, formaldehyde, water and a catalyst.

A theoretical outline of the three-dimensional structure of the resin obtained after the set shows that one molecule of resorcinol reacts with 1.5 molecules of formaldehyde. These theoretical proportions have been verified through experimentation. It has been noted that optimum mechanical properties are obtained from this molecular ratio: resorcin formaldehyde.
If carefully accounted for in the dilution, a disproportionately high amount of formaldehyde will have practically no effect on the grout's principal properties. It must be noted, however, that this surplus of uncombined formaldehyde may come out of the resin after the set and pose toxicity problems. Thus, it is advisable to measure the amount of formaldehyde used carefully, so that it will correspond as closely as possible to the theoretically correct amount.

The second important point in formulating a grout is the proper amount of catalyst. Research has shown that the amount of catalyst to be used corresponds approximately to the amount needed to adjust the pH of the reactive medium. Minimum setting time is achieved with a pH of about 9.3. Pronounced variations in concentration of resorcin-formaldehyde products have little effect on the initial pH of the reactive medium. The proportion of catalyst required to adjust the pH to an optimal level remains practically constant, so that the proportion of catalyst to be used is most often expressed as a percentage.

Thus, formulation for these grouts is quite simple. Since the amounts of resorcinol, formaldehyde and catalyst are clearly fixed, only the diluteness (amount of water) can vary.

Catalysis of these resins, however, involves complex phenomena requiring parameters different from those defined in the initial reaction outline. Unlike industrial resins, phenoplast grouts retain all their constituent products, in particular the catalyst, now chemically attached to the resin, which can form secondary bridges in the network, or even bonds with the skeleton of the grouted soil. Certain additives can also be incorporated into the resin to create such bridges between the grout and the ground. Products of this type are especially in demand for applications in the oil industry (62-30, 62-32, 65-09).

7.31 Viscosity

This is the notable characteristic of these grouts and it is this parameter, rather than the fact that they are organic resin gels, which differentiates them from other types. For most purposes, these resins will have a viscosity of about 1.5 cP. This viscosity is not much affected by the amount of dry matter used. It is also curious to note that viscosity remains practically constant right up to the point of set.
7.32 Setting Time

The setting time of phenoplast grouts is proportional to diluteness: the more dilute the solution, the longer the setting time will be. With very dilute solutions, the setting interval can become very long (> 48 h), with the risk of making the grout unusable.

Products have been suggested for accelerating the setting time (alkaline metal salts or salts of alkaline earths, alkylolamines). With these products, the setting time of highly dilute solutions can be shortened. It should be noted, however, that the cost of these additives can in some instances have a strong effect on the final price of the grout. It is therefore preferable to use more concentrated formulations which give better mechanical strengths, in order to avoid increases in cost. It would also be possible to change the aldehyde, but for economic reasons only formaldehyde continues to be used, since the gain in speed of reaction is not significant with other aldehydes. The same principle is true for catalysts. In some cases it is preferable to use combination grouts: silica gel-phenoplast or lignochrome-phenoplast. In these cases, a fast-setting silica gel or lignochrome is used to produce a false set, with the resin polymerizing subsequently (70-02). Silica gels can be used in weak concentrations and thus do not affect the viscosity of the substance; lignochromes, however, must always be used in large proportions. In both cases, the final properties of the hardened grout are determined mainly by the phenoplast resin.

7.33 Mechanical Properties

In the field of grouting, little research has been done on tensile strengths on pure resins or on resin-sand mixtures as found in treated terrains (VAN LOON 71-06). Similarly, for unconfined compressive strengths, emphasis has always been placed on the behavior of grouted grounds, thus on sand-resin mixtures. As noted above, since ratios of reactive components are fixed, the strength of a resorcin-formaldehyde grout depends on concentration, which is also true for grouted sands. This relationship can sometimes be altered by the use of special catalysts or additives.

7.34 Durability

After setting, the resin retains its dilution water in the form of a colloidal gel. Since this water is not chemically bound, it can evaporate and cause the resin
to shrink. Even if the colloidal gel obtained is somewhat similar to that obtained with polyacrylamide resins, their very different macromolecular structure makes their behavior also very different. As the gel dries out it can contract and crack irreversibly. Thus, for the treatment of ground surfaces where heavy evaporation can pose serious problems, dehydration causes disintegration in the treated ground. The same phenomenon can occur in areas subject to alternating cycles of flooding and drying out, again in the context of the usual range of concentrations recommended. The fact that most of the condensed resin's electrolytes are totally insoluble in water guarantees excellent long-term behavior.

7.35 Toxicity

The raw materials used, resorcinol, formaldehyde and catalyst, are all toxic and caustic and these characteristics must be considered in different degrees during the preparation and the injection of such grouts.

If the resorcin and formaldehyde have been used in the proper proportions, they will have combined completely after the set and become practically inert. Only small amounts of catalyst may sometimes bleed out of the resinous matrix, but only with difficulty because, as is the case with syneresis of silica gels, the resin skeleton is of sand.

7.4 Possible Modifications In Resorcin-Formaldehyde Grouts

7.41 Use of Aldehydes other than Formaldehyde

Other aldehydes may be substituted for formaldehyde. Paraformaldehyde will give comparable results provided it is completely dissolved. Furfural is of great interest because of its plant origin, but its possibilities for grouting have not yet been thoroughly explored.

7.42 Substitution of Other Phenols

DEMINE (71-07, 73-03) patented the use of a rudimentary shale phenol, a product of shale distillation which contains a remarkably high proportion of resorcin-alcoylate derivatives. According to DEMINE, the grout's principal properties (mechanical strength, initial viscosity, and setting time) are good.

GRANIER (65-23) has researched the reaction resulting from a partial substitution of phenol for the resorcin. The substituting molecule inserts itself in the macromolecular network and this substitution process always assumes clearly defined proportions (1 molecule of phenol...
for 2 of resorcin). The usual proportions of formaldehyde and catalyst can be considerably modified in some cases. It is therefore necessary to determine the optimum level of formaldehyde and catalyst for each of these products. In some cases, these products are not sufficiently reactive to permit rapid condensation and, at ambient temperature, mechanical properties can be altered. There is also a toxicity problem. Since the monophenols used are much more toxic and caustic than resorcin, even if very serious precautions are taken at the time of injection, there is still the danger that these phenols may remain partially free after the grout has set.

7.5 Applications

As noted previously, these products have been used in the oil industry and for the treatment of ground surfaces. Even if these injectable resins have been used as grouts, it is essentially because of their low viscosity, which places them, like polyacrylamides, in a distinct category in the range of grouts. Thus, injections of phenoplast resins are used primarily to complement injections of silica gel in the treatment of fine sands and silts.

In defining the principles of grouting and the principal grouts used, CAMBEFORT (61-09) as well as ISCHY and GLOSSOP (62-17) have made note of the first applications of resorcin-formaldehyde for grouting fine and silty sands. The symposium organized in LONDON in 1963 discussed at length the possibilities for these grouts ("Grouts and Drilling Muds in Engineering Practice" 63-03, 63-04, 63-08, 63-37).

Since the original patent was very solid, nearly all applications of phenoplasts have been done by the group SOLETANCHE-RODIO using the resorcinol-formaldehyde process. For many years this resin was practically the only one used on a large scale and has been mentioned in numerous publications (65-01, 65-08, 67-02, 67-04, 69-03, 70-01, 72-02, 74-09).

But it was really in the grouting work done in the Paris Rapid Transit System (Reseau Express Regional, R.E.R.) that the phenoplasts earned their credentials, since some 17,000 cubic meters of Beauchamp sand were treated with more than 5,000 cubic meters of phenoplast grout at the AUBER Station (70-04). It was during this period that ready-mixed products began to appear, such as ROCAGIL (of RHONE PROGIL), GEOSEAL (of BORDEN) and TERRANIER (of RAYONIER), which have been used in Europe and the United States.
Since the phenoplast resins can polymerize in an alkaline medium without being heated, they constitute an interesting, but relatively limited, range of products. Their principal advantages are their low viscosity and the fact that they can easily be used to regulate the strength of the treated ground.

Given the same properties (initial viscosity, grouted ground strength), these resins are still intrinsically more promising than polyacrylamides or aminoplasts. Aminoplasts are only rarely usable. Phenoplasts, which can be used for grouting at ambient temperatures, of course must contain a preponderant proportion of resorcin. Their economic advantage will depend primarily on the price of this product, which has been fluctuating wildly for some years.

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8. CATEGORY A-7: AMINOPLASTS

8.1 Introduction

The first observations concerning the reaction of formaldehyde with urea date back to the beginning of the 19th century. The mechanisms of this urea-formaldehyde condensation reaction are very complex, and thus induced a multitude of theories, none of which has clearly explained the reaction mechanism itself.

It would probably be JOHN (1918) who could claim to have been the first to manufacture resins of this type. Many processes have been developed since then, especially since 1925 when the first industrial urea manufacturing facilities began to appear. This development has been spurred by the fact that urea has become a relatively inexpensive raw material. Aside from molding powders, aminoplast resins have been used extensively in the field of binding materials, paints and glues. Applications in civil engineering, principally for the stabilization of ground surfaces, date from the second world war.

Aminoplast resins harden under heat. Polycondensation of a compound such as urea with an aldehyde (formaldehyde) leads to a stable tridimensional macromolecular network. The solid obtained from the last phase of condensation is practically non-fusible and insoluble. The process of condensation which converts the initial products (urea and formaldehyde, for example) into the final non-fusible insoluble resin passes through successive stages. This conversion from the initial state to the final one can be accomplished in various ways: through single-phase polycondensation or through the use of an intermediate precondensation stage, at which point the resin is still soluble in water or another solvent.

The basic constituents from which aminoplast resins are obtained are urea, melamine, ethylene urea, propylene urea, carbonates, benzaguanadine, aniline and also acrylamide. For the most part these products are inorganic chemicals. The aldehydes which can be used are primarily formaldehyde and its polymers (paraformaldehyde, glyoxal, furfural).

Even though methylolation can take place in either an acid or a basic medium, the final stage is always attained in an acid medium. The study of the reaction mechanism is most complex. Kinetic analysis of the reactions (J. I. de JONG and J. de JONGE, ZADOR) tends to prove that final
polycondensation can take place only in a positively acid medium. This phenomenon explains why all attempts to obtain an aminoplast grout in an alkaline medium or in a medium which is only slightly acid, in order to avoid attacking carbonates in the ground, have never given products which performed well.

In general, the concept of using these resins for ground treatment stems from the extensive use of aminoplasts as glue, essentially an induction and impregnation product. The products recommended for such applications come quite close to what is expected of a grout. The following references concern these grouts and various industrial products and, in a way, constitute the antecedents of the aminoplasts proposed for ground treatment (19-03, 19-04, 24-02, 25-01, 25-02, 28-05, 20-06, 29-08, 30-10, 31-13, 33-11, 34-05, 34-06, 35-07, 35-08, 35-09, 39-08, 39-09, 39-10, 39-11, 39-12, 40-09, 40-10, 40-11, 41-09, 41-24, 41-25, 42-13, 42-14, 43-19, 43-20, 43-21, 44-19, 45-12).

As with the phenoplasts, the oil industry first contemplated using aminoplasts for grouting. Claims have been made for various processes for grouting in connection with oil drilling and oil-bearing strata (44-10). In particular, urea and melamine have been suggested in some patents as partial or total replacements for phenol. These patents have been cited in the analysis of phenoplasts. Most of these processes call for a viscous precondensate, sometimes in solution in a hydrolyzable organic solvent (51-11). Final polycondensation, by preference catalyzed in an acid medium, is accelerated by the high temperature in the injected strata. In some cases, the precondensed resin is in suspension in water (48-20). Furfural thiourea resins have also been proposed for cementing oil-well drill-holes. In this case, the resin will contain sand, bentonite, melamine-formaldehyde, wood fiber, etc. (44-14). For the same purposes melamine-formaldehyde resins containing gypsum have been recommended (49-18).

Reference material covering the use of aminoplasts in the oil industry is much less abundant than that covering phenoplasts. Aminoplasts are especially favored for the stabilizing of ground surfaces. WINTERKORN in particular has researched the various types of resins which can be used for soil stabilization: urea-formaldehyde, urea-furfural, aniline-furfural (45-04). This research indicates that the resin obtained from the reaction of aniline on furfural (47-04) gives the best performances. The bulk of the reference material concerns this type of resin (50-03, 50-09, 50-11, 52-03, 52-07). Although it was specified that these products
were for stabilization, these resins were cited by BEACHES in "Chemical Grouting Report".

MARKUS (55-09) recalls the principal types of resin used for stabilizing soils. Certain types of resins, such as those based on methylolurea and melamine, do not seem very promising because of their poor water resistance. Elsewhere, however, melamine-formaldehyde resins are reputed to be highly resistant to hydrolysis. MARKUS, on the other hand, thinks that sulfamate-formaldehyde-base products are assured a brilliant future. This resin, however, seems to be obtainable only through heating.

8.2 Aminoplasts As Grouts

For various reasons, high viscosity, temperature factor, resin in suspension, these products cannot be considered grouts in the sense used in this survey. These resins have enjoyed only very limited development as grouts because they must be catalyzed in an acid medium. Since most soils are chalky, an acid catalyst is effectively destroyed before it can affect the grout.

Various products and processes have been recommended which would enable condensation to take place in a neutral or slightly acid medium and eliminate the attack of carbonates in those conditions which would otherwise favor such an attack. Thiourea-furfural resins have also been proposed, since they can condense at a pH of 5.5 to 6.5 (43-06), as well as methane-furfural resins which can condense at a pH of 7 (43-13). The characteristics of the end products are not described. It seems, however, that the temperature must be raised before the resin will reach its final state (oil industry applications). Some authors propose urea-formaldehyde aqueous solutions catalyzed in a definitely acid medium, but they make no mention of lime in the ground. In some cases there is an element of ambiguity, as the author speaks of injections for purposes of soil stabilization (65-16).

Since a catalyst whose pH is close to neutral cannot give satisfactory results in calcareous ground, it is necessary to destroy the carbonates by a pre-injection of an acid solution (69-03). This technique is rather costly, increasing the size of the voids which must be treated later, and has not enjoyed much success, except in the U.S.S.R. There is also some danger that the destruction of part of the soil's components may create imbalances. Finally, the acidification process itself may increase the ground's permeability to the point where chemical grouting is no longer necessary.
Based on present knowledge, aminoplast-base grouts are catalyzed in an acid medium and should be injected into ground which is completely free of any elements which might react with the catalyst.

Although many products have been recommended, it seems that only urea, a relatively inexpensive product, is used, the other products being expensive (melamine, thiourea), or hard to handle, mainly because of their toxicity (aniline). Urea is sometimes combined with formaldehyde, sometimes with furfural.

Generally it is recommended that one start with an industrially prepared precondensate, obtained under heat and in an alkaline medium. Condensation is halted while the product is still soluble in water. Final hardening is obtained at the actual worksite through the addition of an acid catalyst. The use of this intermediate stage permits better control of the reaction and avoidance of sudden setting. For example, in France RHONE-PROGIL markets such a resin for grouting in coal mines.

Precondensed resins have also been used in Poland (62-12) and in Hungary, where different types have been examined for viscosity, setting time and mechanical properties (63-24). An examination of these resins' possibilities for injection as well as for surface treatment is included in the general work by GONCAROVE (73-13). With regard to research carried out in the U.S.S.R. on this topic, it would be useful to consult the article by KORZHENKO and MULYUKOV (69-09) which gives interesting figures on successive changes in the pH of a given resin leading to a critical point at which condensation occurs.

In the majority of cases encountered, the use of a precondensate is recommended, but it should be noted that a precondensate will give a product which is more viscous than that obtained from primary products (monomers). Thus, for grouting by injection, one must choose from among all the industrial precondensates those which will give a grout whose viscosity after dilution will be under 20 cP.

8.3 General Properties of Aminoplast Grout

Although little research has been conducted on aminoplast resins for grouting, since possible uses are restricted, the urea-formaldehyde type resins have been researched the most extensively. The reaction process itself and final properties are clearly affected by the dilution of the substance and respective proportions of urea, formaldehyde and catalyst. All other things being equal, optimum
behavior is obtained with a urea/formaldehyde molecular ratio of about one molecule of urea to each three molecules of formaldehyde. A higher proportion of formaldehyde will have little effect on most of the properties.

The more acid the medium, the faster will be the reaction. However, there is an optimum point for mechanical properties which varies considerably according to the catalyst used. Acid catalysis can be obtained through the use of an organic or inorganic acid or an ammonium salt, which, in acting on the formaldehyde (RONCHEZE reaction), releases the corresponding acid. It should also be noted that successive changes in pH during the set are influenced by the type of catalyst used. OGER (68-08) made a rather complete survey of these grouts, in which he discussed the question of catalysis for a certain number of acids and acid salts. The effect of dilution on specific properties of the grouts (viscosity, setting time) was also indicated for various types of catalysts.

8.31 Viscosity

As with polyacrylamides and phenoplasts, viscosity is the parameter which differentiates these grouts from those in Categories A-1 to A-4, if monomers are used. Even when relatively high concentrations of urea are used (200 g/l), the viscosity of these grouts remains comparable to that of water (1 to 2 cP).

For purposes of facilitating control over setting time, in most applications a precondensate is used, thus increasing the viscosity. Therefore, aminoplasts are less suitable for grouting fine soils since they are as viscous as the products in Categories A-1 to A-4.

8.32 Setting Time

Prepolymers can be used to avoid setting time problems, since they permit easy control over this factor but this procedure increases the grout's viscosity.

When monomers are used, the reaction is much more abrupt and setting time is shorter. This setting time is obviously affected by dilution, but it is primarily the choice of catalyst and the proportion of it used which influence the speed of the reaction. Table 11 (OGER 68-08) gives some examples of the effect of the catalyst on setting time if dilution remains constant and the proportions of formaldehyde and catalyst are at those levels which give optimum strength.
8.33 Mechanical Properties

The mechanical behavior of hardened resins has been discussed only in the context of an analysis of unconfined compressive strength of a mortar of siliceous sand saturated with resins which represents the grouted ground. The unconfined compressive strengths of such mortars can vary widely according to diluteness. An example is given in fig. 18, taken from OGER's survey (68-08). It should be noted, however, that it is difficult to obtain good performances from grouts so dilute that they lose their own cohesiveness. As a consequence, aminoplasts are more suitable for consolidation than for pure waterproofing. For a given urea/formaldehyde ratio, these strengths are sharply affected by the nature of the catalyst, and, for a given catalyst, strength attains a maximum and then declines as the concentration is varied. This characteristic, which is highly unpredictable, clearly differentiates aminoplasts from acrylamides. Some examples, drawn from the same survey, are given in figs. 19 to 21. Thus, the catalyst has a direct effect not only on setting time (which is normal), but also on strength, and there is a certain correlation between strength and setting time.

Finally, it should be noted that, unlike other types of resins (polyacrylamide, phenoplast) which form a gel, aminoplasts tend to form a granular solid, which limits their adhesive qualities.

8.34 Durability

If polycondensation is well conducted, one should obtain a resin which is insoluble in most solvents, so it is logical to suppose that the behavior of these grouts over time with regard to their environment should be good. However, there are no known records of long-term behavior.
Fig. 18. Effect of Catalyst Concentration, NH₄Cl, on Compressive Strength of Urea-Formaldehyde
Fig. 19. Effect of Diluteness on Compressive Strength of Urea-Formaldehyde

Urea formaldehyde catalyzed by $\text{H}_2\text{SO}_4$

OGER (68-08)
Fig. 20: Effect of Catalyst Concentration, $(NH_4)_2S_2O_8$, on Compressive Strength of Urea-Formaldehyde

OGER (68-08)
Fig. 21. Effect of Catalyst Concentration, NH₄Cl, on Compressive Strength of Urea-Formaldehyde

OSGER (68-08)
Fig. 21. Effect of Catalyst Concentration, NH₄Cl, on Compressive Strength of Urea-Formaldehyde

OGER (68-08)
for these grouts, aside from successful applications made in Japan as well as in Eastern Europe and the Soviet Union over the last 10 years.

8.35 Toxicity

Before condensation, such grouts require some precautionary measures because of their formaldehyde and acid catalyst content. Processes using a precondensate at the time of preparation contain less free formaldehyde than those using a monomer.

After condensation, the resin is, in principle, quite inert, but it appears that it is difficult to bring the reaction to a point where all the formaldehyde is fixed.

8.4 Applications

For the most part, Western European authors are in agreement with regard to aminoplasts as to the difficulties and limitations associated with their applications (61-08, 67-04, 69-03, 69-06, 72-02, 74-09). However, their possible uses and the technology involved, as well as the results one can expect have been specified (63-08, 69-01, 73-01). Descriptions of applications and their results are mainly from Eastern Europe, principally the Soviet Union (69-02, 69-09, 73-04), and from Japan.

8.5 Conclusion

Aminoplast grouts derived from products such as urea and furfural should be of great interest, as they are not petrochemical derivatives and are made from relatively inexpensive primary products.

Unfortunately, the impossibility of obtaining a grout which hardens at normal temperatures in an alkaline medium seriously limits the situations in which they can be used. However, if preliminary analysis indicates that the ground is compatible with these grouts, they would go to the head of the list because of their relatively low cost.

Moreover, the possibilities of condensation of such resins in a slightly acid medium has been little explored, especially in the presence of furfural derivatives, such as furfurylic acid, and polymers of these derivatives. There is another domain which has been little explored: that of polymerization using a monomer rather than a precondensate. Although the precondensate facilitates control over the final reaction, it makes the mixture more viscous and
therefore less penetrating than those based on monomers.

8.6 Rating

Since aminoplasts use primary products which are relatively inexpensive and not petrochemical derivatives, the overall ratings for Category A-7 are more favorable than those for the two preceding categories. But the fact that catalysis must take place in an acid medium rules out these grouts for calcareous ground. Since their uses are so limited, they have been left out of the general ratings. However, their use should be considered in all cases where the ground to be injected has a low pH.
9. CATEGORY A-8: COMBINATION GROUITS

9.1 Introduction

Many attempts have been made to determine whether it would be possible, by combining two categories, to engineer a grout which could outperform the single grouts which compose it.

The first requirement is that there be no problem of chemical incompatibility, notably, with regard to pH. The second requirement is that the product thus obtained be more desirable from the point of view of quality and price.

9.2 Products Recommended

These two requirements limit the number of grouts in Category A-8 to a very few; there are only two commercial (ready to use) products which fit the definition of category A-8: RHONE-PROGIL'S SIPROGEL and RAYONIER'S TERRANIER.

9.21 Siprogel

Siprogel, patented by RHONE-PROGIL (65-19, 69-08, 72-03) is a combination of sodium silicate and an acrylamide resin. This grout permits both waterproofing and consolidation of the ground.

This combination of a silica gel and an acrylic resin creates variable coriticated networks; they are insoluble, rot-proof. They can expand greatly and are highly elastic. Use of these grouts has been cited for repairing cracks in concrete (72-03) and for consolidating sand (69-08).

9.22 Terranier

Between 1965 and 1970, SOLETANCHE-RODIO began to add sodium silicate or a lignochrome to phenolic grouts (resorcinol-formaldehyde). Their purpose was to make the phenoplast grout set quickly and thus avoid being washed out by underground water (70-02). Since only a small proportion of other substances was added, the fundamental properties of the basic grout (resorcinol-formaldehyde) were barely altered (other than the setting time), so this topic has been covered under Category A-5.

At about the same time, RAYONIER Inc. (U.S.A.) developed and marketed a phenolic grout with a high lignochrome content. It bears the name of TERRANIER (66-05, 68-05, 68-08,
68-15, 68-18). This product truly fits the definition of Category A-8 because it is a combination of A-2 and A-6 type grouts. Its characteristics, before and after polymerization, cause it to resemble the lignochromes: higher viscosity than the classic phenolic resins, poor mechanical performance. J. WARNER (72-04) has made a study comparing TERRANIER's mechanical properties with those of various other grouts (AM-9, silica gels, resin emulsions). Like lignosulfites, these products can react with a dichromate, causing the grout to set. Condensation with formaldehyde, frequently a slow process, takes place subsequently.

Some claims have been made for other products of this type (72-09). In most cases two oxidation reactions are involved (dichromate and condensation with formaldehyde).

9.3 Rating

As a general rule, Category A-1 through A-4 grouts, of mineral or plant origin, are more economical than A-5 to A-7 grouts, since the latter are composed of petrochemical derivatives whose manufacture demands greater delicacy. On the other hand, the category A-5 to A-7 aqueous resins have the advantage over the A-1 to A-4 grouts of lower viscosity, which makes the injection process easier and more dependable.

Thus, any combination of a grout from Categories A-1 through A-4 and a grout from A-5 through A-7 will have the disadvantage of passing into the range of cumbersome products, and of losing the advantage associated with the aqueous resins since the mixture is viscous. This is the case of the two products in Category A-8, SIPROGEL (A-1 plus A-4) and TERRANIER (A-2 plus A-6). However, this does not mean that these grouts are of no interest and are never used. The ease with which they can be used, since they are ready-mixed, and the control over the setting time which they permit justify their use in cases where price is not critical. SIPROGEL is thus frequently used by companies in France in conjunction with the lining of shafts. Whenever seepage threatens the construction of such linings, it can be stopped by a prompt injection of a quick-setting SIPROGEL compound.
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Table 12. Rating Chart, Combination Grouts

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CHAPTER III
COLLOIDAL SOLUTIONS

1. Introduction

Where Chapter II considered the area of true solutions (mineral or organic), this chapter considers organic or mineral colloidal solutions or suspensions. These are divided into two categories: B-1 Organic Colloids and B-2 Mineral Colloids.

Colloidal solutions or suspensions contain particles which are much smaller than a micron, thus injectability is not hindered. All the bentonite-type grouts are included here, since their individual particles do not exceed 1 micron.

However, among all the mineral colloidal suspensions suggested, there are some whose particles exceed 10 microns (clay gel, for example). Such grouts fall outside the scope of this report.

2. CATEGORY B-1: ORGANIC COLLOIDS

2.1 Introduction

A few organic colloid grouts have been patented, but their use is rather limited. Originally they were used mainly as drilling fluids, then later they were found to be useful for ground waterproofing. Those products most used have been alginates, cellulose and its derivatives, casein and grouts based on polyvinylpyrrolidone.

2.2 Suggested Formulas

2.2.1 Alginate Base

An alginate dissolved in water will convert to an insoluble gel either through reaction with an acid (formation of alginic acid), or through reaction with a bi- or trivalent salt (formation of a bi- or trivalent alginate, also insoluble).

The first alginate base formula was introduced by R. J. BALL (39-19), who advocated the use of one or two separate injections of a 17% sodium alginate aqueous solution and calcium chloride, the calcium chloride at 25% of the total, and the alginate solution 75%. Laboratory tests have
shown that such a mixture is much too viscous to be included in a normal category of traditional grouts, although the viscosity of alginate solutions can be lowered by adding peptizers, for example: tannin, humic acid, lignin, wood extracts, alkaline phosphates. However, viscosity rarely goes below 40 cP (40-22). Another cause of the high viscosity of these bivalent salt and alginate base mixtures is that they thicken somewhat as soon as they are prepared (the beginning of the salts' reaction on the alginate). It would be possible to use a delayed action coagulating reagent, (which would also be true for hard gels).

SOIL MECHANICS Ltd. has patented a mixture of this type: an alginate solution plus 1% calcium chloride plus 1% ethyl acetate. The ethyl acetate hydrolyzes into ethanol and acetic acid, which releases the alginic acid and forms a gel in the ground (61-26).

Combining a peptizer and a delayed action coagulating reagent is also possible. M. DOWELL suggested sodium alginate, ammonium phosphate, formaldehyde (62-24). The advantage of the alginates is their modest cost, but they tend to be too viscous.

2.22 Cellulose Derivative Base

These grouts produce a gel which gives good waterproofing results and is neither corrosive nor toxic. LOOMIS (36-18) suggested colloidal solutions of viscose (in a slightly acid medium), cellulose acetate and nitrate (in a diluted acetic acid solution), nitrocellulose and hydroxy-ethyl cellulose (in a slightly basic medium).

WAGNER (48-17) suggested treating soil with an aqueous solution of sodium carboxymethylcellulose salt. This solution may or may not be mixed with another salt, often calcium chloride, but this second salt may also be ferrous sulphate, ferric chloride, or barium nitrate. It is not always necessary to add a coagulant, since the natural salts present in the formula's water are enough to precipitate the sodium salt from the carboxymethylcellulose.

2.23 Starch Base

GREBE (35-11) suggested injecting an aqueous solution or dispersion of fine powdered starch, prepared from rice flour, for example, to form a gel in the ground. The solution would use 1 to 10 parts starch for 90 to 99 parts water.
2.24 **Protein Base**

GREBE (35-11) also suggested using a protein such as gelatin as a base. The grout's consistency and the time it takes to harden depend on its initial concentration. The gel, once formed, risks being destroyed by soil bacteria and micro-organisms.

2.25 **Casein Base**

HART (40-27) advocated the use of an alkaline dispersion of casein to which lime hydrate is added, but this grout is too viscous. An improvement was made through injection into the ground of an aqueous ammoniacal solution containing 3 to 4% casein and then formaldehyde at 20 to 60% of the casein. The resinous and viscous result of the condensation ensures the formation's watertightness (VONDERAHE 44-08).

2.26 **Polyvinylpyrrolidone Base**

For this grout, rather viscous 10% aqueous solutions are used. Then, hydrogen peroxide and hydrazine are added. After an interval which can be regulated (from 20 or 30 minutes to several hours at ordinary temperatures), a plastic gel impervious to water (99-07) is formed.

2.3 **Rating**

In theory, these grouts can be used for the waterproofing of sandy formations but not for their consolidation. Viscosity is always rather high and their price higher than that of silica gels, which limits their use. In addition, they risk being destroyed subsequently by soil bacteria.

Their principal advantages are that they are non-toxic, not petrochemical derivatives, and usable in small quantities, which reduces preparation costs.
Table 13. Rating Chart, Organic Colloids

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Not usable
3. CATEGORY B-2: MINERAL COLLOIDS

3.1 Introduction

Clay grouts (without cement) have been used for a very long time for grouting fine terrain. Such grouts fit neither the definition of a colloidal solution (since these suspensions are made with finely ground, but not colloidal minerals), nor do they fit the precise definition of a "chemical grout." They are covered in this report for two reasons:

a. They are the ancestors of the bentonite grouts, which can be legitimately classified as "chemical grouts",

b. As intermediate products between cement grouts and chemical grouts, these clay grouts are most useful on alluvial soils. Numerous examples attest to this fact: LAC NOIR dike, France (62-18, 62-28); FESSENHEIM Plant, France (55-08, 62-28); NOTRE DAME DE COMMERS Dam in the Alps (62-18, 65-12); ASWAN DAM (65-13); SYLVENSTEIN Dam on the Issar, Germany (62-17, 62-18); BOU-HANIFA Dam, Algeria (62-18); Hydroelectric plant at FINSING, Bavaria (62-28); MANGLA Dam, West Pakistan (63-02); MISSION Dam, Canada (74-09).

In these examples, clay was not used in its pure state because such a grout would not attain an adequate consistency over time. It must be rigidified with silicate, generally used in conjunction with calcium chloride or sodium aluminate (63-31). Since these products are powerful clay flocculants, the mixture formed is heterogeneous, producing a liquid phase which sets, then a clay phase which has difficulty penetrating into the ground.

The use of a selective peptizer, of the monosodium or monopotassium phosphate type, is preferred as it permits an extension of the injectability of these grouts, but these grouts are always less injectable than bentonite base grouts. The centrifugation of the clay in a hydrocyclone has also been suggested (63-12).

3.2 General Characteristics of Bentonite Grouts

Bentonite grouts do not share the shortcomings of the clay grouts: no more than 4% dry matter is used, the
particles are small enough to allow their use on fine soil, and to prevent any appreciable sedimentation during injection. Bentonites are formed through an alteration in volcanic ash. The particles are less than 1 micron in size (63-11, 63-31). Suitable bentonites are rarely found in Europe, and various methods have been developed for the use of local bentonites (50-02). Domestic bentonites are mainly found in Wyoming and vicinity.

Their chemical structure enables the bentonites to absorb large amounts of water. They have the privilege of being thixotropic, that is, of becoming fluid when agitated and changing into a gel when at rest. This attribute is very important in a grout which will be required by definition to solidify quickly and permanently when placed in the ground. The gels obtained, however, are not strong enough to make the ground very hard and they are used exclusively to reduce permeability.

To identify the properties of bentonites, one first observes the active surface, which is determined by the surface of the particles in a given solid mass, this surface area being expressed as a specific area in cm² out of a total surface area per gram of solid (BLAINE Test), and proportional to the fineness and the form of the particles.

The plate-like crystal lattices of the clay minerals are made up of sheets of silica and alumina whose surfaces have unsatisfied valency bonds, which are the sites for the fixing of ions. Typical ions are lithium, hydrogen, sodium and calcium which have differing abilities to surround themselves with water molecules. It is this water of hydration which produces the swelling of particles (63-11).

The montmorillonites, which have a triple-layered lattice, are able to bind ions and thus absorb water between the silica-alumina sheets as well as on the outer surfaces of the particles, and thereby expand more than the double-layered lattices of the kaolinite and illites groups (63-11).

Isomorphous replacement of magnesium for aluminum in the octahedral layer, or aluminum for silicon in the tetrahedral layer, causes a net deficit of electric charge within the crystal which may thus be regarded as negatively charged and the exchangeable cations are located on the clay lattice without penetrating deeply (61-16).
Dry bentonite contains oriented elements. Addition of water causes interlamellar swelling. A regular increase in the distance between crystallites occurs as more water is introduced. This swelling is reversible and its final extent is governed by the nature of the exchangeable ion and by the liquid used to promote swelling. The calcium exchanged bentonites swell less than suspensions of pure sodium bentonite which can show virtually infinite swelling in water of low electrolyte content.

The colloidal character of the bentonites allows them, with a small amount of dry matter, to produce a suspension which is viscous but highly injectable. The flowing properties of these grouts have been tested in laboratories with capillary tubes. The apparent permeability of the sand to be treated is approximately inversely proportional to the grout's viscosity.

3.3 The Setting Process

From the above considerations, it emerges that bentonite grouts must set in a given time and that the resulting gel must be stable. This process may take place directly, or with the assistance of other reagents: anti-flocculants, rigidifiers, etc.

The viscosity of bentonite suspensions is set at between 15 and 20 cP, indicating that from 35 to 60 kg/m$^3$ of dry matter will have to be added depending on the quality of the bentonite (fineness and nature of the surrounding ions). In a fresh grout, the mixture's rigidity is very low and does not hamper its penetration in the ground. This rigidity increases with time, the grout sets and permanently waterproofs the fine ground.

This direct process (without an additive) has been used occasionally, and its basic idea was incorporated into the technique of jet grouting (YAHIRO and YOSHIDA 74-01).

As noted above, the individual particles of bentonite are less than one micron in diameter. But, if the water contains electrolytes, or if the ground to be treated contains soluble salts, the individual particles of bentonite stick together in floccules whose size can reach and even exceed 10 microns, thus hampering the grout's penetration into fine soil. CARON's studies (70-07) indicate that there is a connection between the range of a grout in a given terrain and this state of flocculation.
The most classic procedure for the deflocculation of bentonites is the use of peptizers or deflocculants. Deflocculated bentonite suspensions present no problems of injectability and can be used to grout fine sand. The first patent in this field dates back to 1943 (SULLIVAN 43-11). The process involves two steps: first sodium tetraphosphate (from 0.25 to 10% in aqueous solution) is injected, then the bentonite. Flocculation caused by ions in the ground is thus avoided. In addition, the bentonite grout used in the second step contains calcium montmorillonite which, as it converts to sodium montmorillonite in the ground, will absorb additional water since the sodium form is more hydrophilic than the calcium.

But since this process involves two steps, with all the disadvantages inherent in such an approach, it does not seem to have been considered often. Subsequently, CARON (55-14) showed that exactly the same result could be obtained with only one step: a fine sand (with particles ranging from 0.1 to 0.2 mm) was successfully injected with a suspension containing 10 kg of bentonite diluted with 100 litres of water to which 1 kg of sodium pyrophosphate had been added. This simpler method has been used a few times, for example at the ASWAN Dam in Egypt.

CARON (55-14) has also described another way to increase the penetrability of bentonite grouts in soils with low granulometry. This procedure consists of bringing about the formation of stable gas bubbles in the grout. Suspendsibility is improved by the gaseous emulsion, and the replacement of a large proportion of the grout by air or a gas does not lower the watertightness of the ground thus treated. The foaming agent most often used is a tensioactive substance, such as a sulphonated fatty alcohol, and the gas-producing agent, aluminum or calcium carbide.

Attempts have also been made to improve the gel's cohesion in the ground by increasing the concentration of dry matter. To achieve this end, it has been suggested that the hydration of the bentonite be delayed.

A procedure described in 1936, and taken up again by VAN LEEUWEN in 1940 and the years that followed (40-15, 42-12, 43-09, 43-16), involves delaying the solvation of the bentonite until it is thoroughly in place in the ground. The bentonite is covered with a fine hydrophobic film, usually petroleum, then placed in suspension in water and finally injected into the ground. Other procedures give the same result by using the bentonite grout in conjunction
with a coagulating solution. Since these are combined processes, they will be analyzed in Category F.

3.4 Applications

Injections of bentonite in suspension have been used in the construction of various wells or tunnels, or for the creation of watertight screens under earthen dikes (57-16, 62-29, 62-28, 74-09).

These grouts were usually used in alluvial soil, in the period after the cement-clay era and before the silicates. However, when the soil to be grouted is made up of different layers of fine, medium and coarse gravel and sand, all irregularly distributed, cement-base grouts can only fill the larger gaps, and it is necessary to complete the treatment with a product with better penetration. This can be a true solution of the silicate gel type, but it is often wise to intersperse those two treatments with an injection of bentonite.

3.5 Rating

These grouts are inexpensive, especially if bentonite is found in the area of the construction site. As with all clay-based grouts, bentonite grouts are very durable, whether attacked by water or subjected to ground buckling, because of their high plasticity.

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CHAPTER IV
NON-AQUEOUS GROUTS

1. Introduction

Nearly all grouts in use are aqueous (true solutions, colloidal solutions, emulsions), for reasons of ease of handling, safety, economy. The capabilities and diversity offered by aqueous formulations makes the use of non-aqueous formulations pointless in most cases. However, since non-aqueous grouts do exist, they have been included in this report in the following categories:

C-1 Synthetic resins
C-2 Vulcanizable oils
C-3 Asphalt and other heated compounds
C-4 Formulations using solvents

These four types of non-aqueous grouts have been used for very limited and specific purposes in the past and can also be used in the future. However, their limited range of applications prevents their inclusion in Categories A or B. The ratings for non-aqueous grouts compare poorly to those of Categories A and B.

a. They are all expensive, with the possible exception of Category C-3 in unusual cases.

b. They are all highly viscous, except Category C-4 in some cases.

c. They are all flammable and often dangerous to handle.

d. They are all petroleum derivatives.

e. Most important for normal grouting purposes, they do nothing that the cheaper and less dangerous Category A and B grouts cannot do.

2. CATEGORY C-1: SYNTHETIC RESINS

2.1 Introduction

There are grouts which use synthetic resins in a pure state, without solvents or dispersants. The use of diluents is to be noted, however, but here the product can
polymerize with the basic resin and thus does not serve just as a solvent.

In general, these resins are plastic substances which harden by thermal reaction and pass from a liquid to a solid state at ambient temperature. Since they do not contain solvents, these products are expensive and thus can be used only in exceptional cases, where there is limited area to be grouted and high mechanical properties to achieve.

These resins can be considered more as glues than as grouts. Many glues can be used for grouting, but these products, whose appearance in the fields of public works and building construction is of recent date (about 1960), have enjoyed only limited applications up to the present.

With regard to injectable resins, it seems that only products in the following families have been recommended: polyesters, polyvinyls, epoxy resins, polyurethanes, furan.

2.2 Polyester Resins

As their name indicates, these resins are obtained by combining a polyacid with a polyalcohol. Those resins used in grouting are unsaturated,

In most cases, polyester resins are obtained through condensation of an unsaturated diacid (maleic or fumaric acid) with a dialcohol. But there are also resins obtained from unsaturated bases with alcohol (allyl alcohol). The polyesters thus obtained are highly viscous, even solid, and yield only mediocre products after polymerization of the radical. Thus, commercial products consist of a basic polyester diluted in a reticulant. This reticulant is an ethenyl, acrylic or vinyl monomer, with styrene the most often used. Commercial polyesters contain 30 to 40% styrene which allows the use of resins whose natural viscosity will range from some hundreds to some thousands of centipoises.

Polymerization is obtained through the addition of a catalyzing substance, containing a catalyst of peroxide type and an accelerator which facilitates the decomposition of the peroxide into free radicals. This accelerator may be a cobalt salt, a manganese salt, a vanadium salt, a
tertiary amine, a mercaptan, or a quaternary ammonium salt. The formulations can be varied infinitely by varying the quantity and quality of the basic polyester used (acid and alcohol), the diluent, and the catalyst (67-01).

The catalyst as defined above causes the polyester resin to polymerize and copolymerize with the reticulant (styrene), to form a gel in the first phase, then a hardened polymer. As the substance turns from a gel to a hardened resin, it gives off a great deal of heat. The time needed for gelling and hardening can be varied from a few minutes to several days by varying the amounts of catalyst and accelerator used. But it should be noted that these resins can contain volatile compounds, which makes long setting times uncertain.

The basic resins found on the market have a minimum viscosity of 200 to 250 centipoises (70-03), which is rather high and rules out the use of these products for grouting sand. Thus, users have endeavored to lower initial viscosity to between 10 and 50 centipoises by increasing the amount of reactive diluent (99-07, 70-09). Because of shrinkage of the mass of grout, this method is inapplicable to resins poured into large size voids, but it can be used in injections, since the resin is divided up and the ground serves as support.

By 1941, MATHIS (41-16) was advocating the plugging of cracks and porous formations in non-acid terrain, such as dolomites, in conjunction with oil-well drilling. He uses a resin formed by condensation of a dicarboxylic acid, maleic acid for example, with a polyalcohol: ethylene glycol with or without vinyl acetate in the presence of benzoyl peroxide as catalyst.

The properties and conditions for use of these resins have been researched in laboratories (63-08, 63-20). These grouts will impart to the treated ground high performances comparable to those of concrete (300 to 400 bars on fine sand). The relatively low elasticity of the pure resin (modulus 15,000 to 30,000 bars) allows it to absorb the internal stresses due to shrinkage rather well (64-13, 70-03, 99-07). The treated sand is obviously more elastic. CARON (70-09) has defined the general principles governing the formulation of grouts for use in fine cracks: depth to be penetrated, size of opening of the fissure, conditions of moisture and cleanliness.
The long-term behavior of these resins can be considered good to the extent that they are sheltered from ultra-violet rays, but there is always a long-term risk of hydrolysis, especially if the medium is alkaline (99-07). With regard to toxicity, certain precautions must be taken during preparation, but after polymerization, the risks are reduced. Some polyesters are guaranteed to be non-toxic (foodstuff quality), but the addition of reactive diluents can alter their behavior.

These grouts have been used principally for the treatment of cracks in buildings and works of art: dams, bridges, trussed or prestressed beams (64-13, 69-03). They have also been used in mines, in particular for the consolidation of gallery roofs. Polyesters have also been used to grout underground rivulets in salt mines, a very appropriate application, since their formulas contain no salt solvents. Polyester grouts have also been used to treat porous and fissured rock (68-11). A most spectacular application of this product was the consolidation of the stone-work of the ABU SIMBEL temple on the Nile (67-02).

Polyesters have been used rarely and in small quantities for the treatment of sand. They have been used to treat the ground around existing foundations (micropilings, for example) in order to increase load-bearing capacity (67-01).

In conclusion, polyester grouts give very good performances which far exceed the traditional classic standards for grouts, but they are expensive (as they are not diluted) and thus suitable only for very specific applications. If rated according to the definition used for grouts as a whole, polyester grouts would score very low, especially since they are petrochemical derivatives.

2.3 Polyvinyl Resins

These resins bear some similarity to polyester resins, polymerizing in approximately the same way. Many vinyl compounds can form a polymer, and they are used widely on an industrial basis. For grouting, the products recommended are primarily acrylonitrile, vinylidenechloride and styrene. Only styrene and vinylidenechloride seem to have been developed, principally in the oil industry (40-25, 42-08, 42-10, 47-07). Their injectability and behavior in the ground have also been examined (47-02). It has also been suggested that an injection of styrene-base
grout be followed by an injection of a plugging type grout, of the organic gel group (40-24, 40-31).

The triggering of the polymerization reaction in a vinyl monomer requires a far higher energy level than is necessary for polyesters, and, at normal temperatures, the usual peroxide and cobalt salt catalysts have no effect. This is why these grouts are used almost exclusively in conjunction with oil-well drilling where they can take advantage of the high temperatures prevailing in the strata to be injected. At the present time, it appears that these grouts have not been used for traditional grouting.

2.4 Epoxy Resins

Like the resins described above, epoxy resins harden under heat, but, unlike the preceding examples where hardening is obtained through polymerization, in this case it is attained through the addition of a reagent, called a hardener. For polyesters, setting time can be varied by increasing or decreasing the amount of catalyst, while for epoxy resins, the resin-hardener ratio can be varied to a much smaller extent.

In general, the epoxy resins commonly found on the market are derived from the action of epichlorhydrin on Bisphenol A (2,2- bis (4- hydroxyphenol) propane). A wide variety of resins can be obtained through varying the proportions of epichlorhydrin and Bisphenol A.

These resins can be hardened by amines, polycarboxylic anhydrides or monocarboxylic acids. The respective proportions of resin and hardener are defined stoichiometrically in terms of respective reactive groupings of the two components. Although an additional polymerization reaction is the method most frequently used, it should be stipulated that epoxy resins can polymerize through the action of a catalyst (alkaline, LEWIS' acid). The multiplicity of basic resins and hardeners available permits practically limitless variations in the formulas.

The most fluid of the basic resins have a viscosity of at least 400 cP. A carefully chosen fluid hardener, if added in significant quantities, enables this viscosity to be lowered to about 100 cP (70-03, 70-09, 72-03). The grout can also include reactive diluents such as butyl glycidyl ether, butane-diol-diglycidyl ether, cresyl glycidyl ether. With these products, viscosity can be lowered to
about 20 cP.

The behavior of these resins in applications in the field of public works has been studied with particular attention to the effects of temperature and moisture (65-06, 67-01, 70-14). The general properties of this grout in the ground are rather similar to those obtained with polyesters. The setting time depends on the choice of hardener and is difficult to regulate. Mechanical properties are superior, durability is excellent. Even if some precautions must be taken at the time of injection, it is still possible to obtain hardened resins with maximum guarantees against toxicity.

These resins have been used primarily for glueing, sealing and the treatment of cracks in rock and concrete (59-08, 62-31, 63-21, 64-16, 67-01, 70-09, 70-10, 70-11, 70-13, 70-15, 70-16, 70-17). The regeneration of fractured rocks has also been achieved with these grouts (64-14, 68-11). Finally, epoxy resins have been used for grouting rather open ground around foundations in order to increase their loadbearing capacity (67-06, 68-16). In conclusion, these grouts have been little used for soil grouting because of their very high cost (67-06, 69-03).

2.5 Polyurethane Resins

The reaction process with polyurethanes is comparable to that encountered with epoxy resins. The reaction resulting in a hardened product consists of an addition polymerization between an isocyanate and a compound containing hydroxyl groups, such as a polyalcohol or a polyester. The choice of isocyanate and the hydroxylated compound determine the product's viscosity. One of the characteristic properties of these products is that the isocyanate function reacts with water, releasing carbonic gas while doing so, and leads to a cellular structure. Since a part of the isocyanate is destroyed in the course of this reaction, the original formula must include a slight overdose of it to compensate for the loss.

Since water is almost always present in the ground, this reaction takes place in the ground and so polyurethane-derived formulations will be examined under Category E-2 (Reaction with Groundwater).
2.6 Furan Compounds

Like the various synthetic resins examined above, furanic compounds are normally prepared without being diluted with water. Thus, they have the same economic disadvantages and, consequently, pure furan resins can hardly be contemplated for grouting.

However, some resins in the furan group are compatible with water and these diluted formulations can be of interest. They have been included under Category A-4.

2.7 Conclusion

The cost of grouts described here in Category C-1 is prohibitive in comparison with most other grouts. Their use is reserved exclusively for special works where very high mechanical performances, comparable to those of traditional concrete, are sought. For this work, polyesters would be preferable as they are three times cheaper than epoxy resins. The latter are used only in those cases where a polyester would risk being rapidly hydrolyzed by the medium.
3. CATEGORY C-2: VULCANIZABLE OILS

3.1 Introduction

It is possible to use unsaturated oils which can be made to polymerize without being heated, through the addition of sulfur chloride (LERCH 40-23), to produce a particularly elastic waterproof mass. Because of its close relation to rubber, one can speak of "vulcanization." This product is marketed under the name of POLYTHIXON by PEUTE CHIMIE.

3.2 Limitations

This product is rather viscous before setting and can be injected in depth only under rather high pressure. CHAMBERLAIN (41-23) suggested that penetration could be facilitated by a preliminary injection of a water-soluble solvent (alcohol, ketone, etc.).

Since the "vulcanization" time is rather long, there is some risk of leaching just after injection, but this risk disappears completely after two days and permeability decreases despite the loss of a certain part of the grout through leaching (70-02).

3.3 Applications

The grout has been successfully used for various waterproofing problems, particularly in gas or oil wells where waterproofing was connected with risks of corrosion.

3.4 Conclusion

Because of their high price, these grouts have not been developed for extensive applications. Their advantage, for special cases, lies in the fact that the grouted mass can remain fairly supple. However, for this purpose the acrylamides (Category A-5) give the same results, allow greater latitude in the regulation of setting time and have the advantage of greater fluidity.
4. CATEGORY C-3: BITUMEN AND OTHER HEATED COMPOUNDS

4.1 Introduction

Substances in a molten state can be applied to porous formations for waterproofing and consolidation, but this process is difficult to use as it requires special heating equipment with precise regulation of temperatures (30-11, 31-15, 32-10, 69-12). In addition, it is often necessary to preheat the ground by steam (06-01, 21-01, 41-12, 41-13) or to ensure the circulation of warm grout in a closed system within the grout hole (K. R. DEMFWOLFF 69-12).

Despite this advance heating, the penetration range of this product is short in sand, so this process is used primarily for coarse formations, for filling crevasses and cavities or for joining concrete dams (53-01). This type of grouting has been used on dams in Alsace, at HALES BAR GUILD in Tennessee and at GREAT FALLS on the Canvey Fork (71-05).

Thus, Category C-3 products do not really fit the definition of a chemical grout for use in slightly permeable soils.

4.2 Suggested Products

Among the possible products, the following have been suggested: paraffin (00-02); naphthalene (21-01); sulfur (41-12, 41-13); metals such as bismuth, lead, tin, cadmium, antimony, zinc (41-22, 42-11); and finally, and above all, bitumen (30-11, 31-15, 32-10), which is the only product to have been used (53-01, 69-12, 71-05).

4.3 Conclusion

For waterproofing of soil by grouting, the grouts of Category C-3, mainly bitumen, theoretically present two advantages: there is no dosage to regulate since only one product is used, brought to the proper temperature; and these grouts possess great chemical inertia.

However, the difficulty of placement (because of the necessity of heating) and the short range of penetration in fine soils render these grouts rather unsuitable for this range of applications, and no rating is given.
5. CATEGORY C-4: FORMULATIONS USING SOLVENTS

5.1 Introduction

In certain rather rare cases, use has been made of the products mentioned in the preceding chapters, but diluted with non-aqueous solvents and thus rendered less viscous. Bitumen and epoxy resins have been similarly diluted using an aromatic type diluent insoluble in groundwater.

Although they obey a totally different principle, it would be appropriate at this point to note those procedures which use a water-soluble solvent (of acetone or alcohol type). In this case, the diffusion of the solvent in groundwater during injection causes the dissolved matter to precipitate. This sort of process will be examined in Category E-2 (Reaction with Groundwater).

5.2 Bitumen in Solution

This process has been used to waterproof, and sometimes to consolidate, porous formations and sand. It offers the advantage over emulsions of avoidance of premature breakdown of the emulsion. It can thus penetrate deep into the ground and is fairly economical.

The bitumen is dissolved in a solvent such as kerosene and forms a fluid solution which, 24 hours after injection into the ground, forms a mass which resembles a gel (41-28). It is possible to add sulfonates or naphthenates to enhance penetration of very fine pores. A very fine solid, such as lime or clay can also be added to reduce cost (41-28).

5.3 Epoxy Solutions

Epoxy resin solutions have been successfully used in oil wells to waterproof and consolidate sandy formation. In cases where this grout was used, the secondary purpose was to permit the flowing of oil. This process is generally inconceivable for traditional types of grouting.

HILTON and SPAIN have obtained excellent compressive strength and sand adhesiveness by two successive injections of low-viscosity solutions (5 to 25 cP). The process is as follows: after removing the water from the formation, one first injects an epoxy resin solution (from
60 to 90%) in a mixture of ethanol, methanol and kerosene containing some aromatic hydrocarbons, which give a clear homogeneous solution (other solvents are also recommended, such as diesel oil with toluene or acetone), then a second solution containing the hardener diluted with kerosene or diesel oil. The first solution drives out any residual water and the resin covers the grains of sand, then the second solution containing the hardener forces the first solution deeper into the ground and causes the epoxy resin to set (63-36).

ROBICHAUX also advocates the preliminary elimination of water from the formation by diesel oil or by kerosene followed by isopropyl alcohol before proceeding to inject the epoxy solution with its hardener (generally amine). The solvent will be of the aromatic group such as benzene or kerosene (64-20).

5.4 Conclusion

Thanks to the presence of a solvent, these bitumen or prepolymer-base mixtures are of sufficiently low viscosity to be easily injectable. Since the solvent will disappear from the grout sooner or later, this sort of product cannot ensure good long-term watertightness. The product is thus limited to purposes of consolidation where waterproofing is not necessary.

Because the solvent is organic, this type of grout is dangerous to use (risk of fire, explosion, respiratory intoxication, etc.). Finally, the Category C-4 grouts are relatively costly and entirely based on petrochemical derivatives and so no rating has been given.
1. Introduction

An emulsion is the suspension of very fine drops of one liquid in an immiscible liquid, one phase of which is generally water. There is one continuous phase and one dispersive phase. A direct emulsion is one whose continuous phase is water and a reverse emulsion is one for which water constitutes the dispersive phase.

Emulsions used in grouting are of the direct type, of which the best known example is bituminous emulsion. A viscous liquid, such as bitumen, dispersed in water results in a liquid with fairly low viscosity which is then used for injection into less permeable soils.

If necessary, the fluidity of a direct water emulsion can be increased by adding water. It should be noted that with a reverse emulsion the opposite effect occurs, the increase in the concentration of the dispersive phase leading to a thickening of the system. This property is useful in creating a grout which can thicken on contact with groundwater. This will be covered in Chapter VI. This chapter, however, will deal only with direct emulsions, namely bituminous emulsions and other emulsions.

These direct emulsions break up on contact with the ground. The two elements separate and the more viscous settles and fills the ground pores. The addition of a destabilizing agent can also be used to assure the breakdown of an emulsion.
2. CATEGORY D-1: BITUMINOUS EMULSIONS

2.1 Introduction

The bitumens used are coal-tar or asphalt base and the emulsion is strongly stabilized (casein, for example). This procedure can be used successfully in fine grain clayey sands (38-10, 53-01, 65-08, 73-13). It allows the permeability of the soil to diminish but has little effect on cohesion (strength). It cannot be used in coarse soils because of the risk of having badly gelled emulsions draw away.

2.2 Method of Breaking Down Emulsions

2.21 Direct Breakdown

This happens by breakdown on the grains of the ground or by elimination of the stabilizing agent (protective colloid agent), which can either decompose or be absorbed by the fine elements of the soil. But, for this to happen, proportioning of the stabilizing agent must be very precise. This procedure is not entirely satisfactory since proportioning is difficult to control and the emulsion can break down too quickly or too slowly.

In order to lessen the risk of breaking down too quickly, it has been proposed to first complete an injection of sodium tetrapyrophosphate (43-11). The second risk can be lessened by first injecting a stabilized bituminous emulsion, followed by a less stable emulsion which would cause the whole to coagulate (36-19, 39-25).

2.22 Breakdown by Addition of a Destabilizing Agent

The agent used can be added after injection, via the bituminous emulsion. This method would use a gas (CO₂ or Cl₂), and has been cited by ASKALONOFF (38-01, 38-02).

However, one-step methods are preferable. Therefore, the following additives have been proposed:

electrolytes: VAN HULST (37-18), or more specifically, bi- or trivalent salts, such as calcium chloride (ASKALONOV 38-01, 38-02), calcium or aluminum sulfates (MCKAY 37-17).
amine with high molecular weight, or quaternary ammonium (MILES 45-08).

hydrolyzable esters: formiate or ethyl acetate or methyl acetate (38-02, 38-01, 40-30, 50-02, 32-12, 38-06, 53-01, 58-04, 67-02).

2.23 Breakdown by Adsorption of Part of Emulsifying Water

A stable bituminous emulsion contains 50% water; if the percentage diminishes to 20% or 30%, the emulsion breaks down. In the ground, an emulsion cannot dry up by itself and a chemical reaction must be found to absorb much of the water, occurring as a delayed reaction. This can be done by adding sodium silicate and a gelling reagent such as an aqueous resin (CARON 52-16). After the system takes effect, the excess water becomes an integral part of the grout, which develops a rigidity not possible with pure bitumen. Samples of sand treated this way were submitted, without washing, to water pressure of 7 kg/cm² (100 psi).

SOMMER and GRIFFIN (55-12) have proposed a similar formula: bituminous emulsion stabilized by a salt of sodium of pine resin plus sodium silicate, with a ratio of 2/1, plus acetic acid.

Certain finely divided substances, often in a colloidal form, have been added to bituminous emulsions: diatoma (37-18); bentonite (37-18, 38-06, 39-07, 43-11); hydroxide of aluminum, iron or tin (39-07); organic substances such as humic acid, gelatin or starch; latex (40-14). These products are added to improve the performance of the bituminous emulsion (for example, latex), or to enable their use in open soils.

Finally, a bituminous emulsion grout can be aerated in order to add a thickening agent which stabilizes the foam during the liquid phase (CARON 53-13).

2.3 Applications

Application is aimed solely at imperviousness of fine sands (dunes, for example) or of finely fissures masses (38-10, 58-04, 71-05, 74-02).

2.4 Rating

Bituminous emulsions have as their advantages
their relatively low price, ease of placement, good long-term stability and non-toxicity of ingredients.

However, unless a silicate or an aqueous resin is added, their breakdown is unreliable, and only a weak cohesion is conferred to the ground. These products are therefore reserved for waterproofing.

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3. CATEGORY D-2: OTHER EMULSIONS

3.1 Introduction

Other aqueous emulsions are conceivable for grouting, although their use has been much more limited than that of bituminous emulsions. The following have been cited: emulsions of epoxy or polyester resins, vinyl emulsions, natural latex and paraffin wax emulsions.

3.11 Emulsion of Epoxy and Polyester Resins

Because of their high price, these emulsions have never been widely used (62-17, 72-04). Their only advantage is that they can be used for consolidation of fine soils, while such an application is not generally possible with bituminous emulsions.

Certain relatively new formulas of polyester, of the type 2 hydroxyethyl methacrylate of diethylene glycol, may have an interesting future.

3.12 Polyvinyl Emulsions

These emulsions of polyvinyl alcohol or polyvinyl acetate in water have been suggested for the stabilization of sandy soils (59-06, 74-02) or for concrete repair (70-12), but these products are easily diluted in water. Therefore, it is necessary to add water-repellant products such as certain natural oils or vinsol (MARKUS 55-09).

Various patents have established the polymerization of acrylonitrile emulsions (54-12, 55-11, 56-12, 56-13), but these have not apparently been used for injection into soils.

3.13 Latex

It is possible to fill ground formations with emulsions of latex in water, which are very flexible and water-resistant (MUNAY 52-03). One can ease the introduction of the grout by first injecting a solution of sodium tetrapyrophosphate (43-11).

3.14 Emulsions of Paraffin Wax

These emulsions in water must be very fine and are used for soil waterproofing by adding a dispersing
agent of polyvalent metal, such as aluminum formiate, zirconium acetate or aluminum acetate (63-35).

3.2 Rating

Because of their decidedly higher prices, the grouts of Category D-2 have seen much less use than those of Category D-1 and there are, accordingly, fewer studies available on them. There is also very little information on formulations to be used concerning performance or durability. Thus, the figures given in Table 16 are uncertain.

As this category contains several rather closely related types of products, for the rating the two most interesting products are:

in waterproofing: natural latex, since it is not derived from petroleum;

in consolidation: polyester emulsion, the only product in Category D that can be used in consolidation.

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<th>Table 16. Rating Chart, Other Emulsions</th>
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CHAPTER VI

PRODUCTS REACTING WITH THE GROUND

1. Introduction

In all the preceding formulations, with a few rare exceptions (colloids, heated bitumen), the grout needed a reagent (for gelification, polymerization, etc.) to pass from a liquid to a solid phase and this necessity required: either that the work be carried out in two phases (first the grout, and then its reagent would be successively injected into the ground), or that the reagent be introduced at the time of preparation, while necessary measures were taken to ensure that the grout would not set too rapidly.

Thus, it seems logical to try to take advantage of the ground (or the water in it) to bring about the set in situ. In this case, one must choose a grout which will react with salts in the ground or in groundwater (provided that the one or the other contains suitable salts) or a grout which will react with water itself. This chapter deals with two types of grouts:

Category E-1 Reaction with Ground or Groundwater Salts

Category E-2 Reaction with Groundwater

2. CATEGORY E-1: REACTION WITH SALTS IN GROUND OR IN GROUNDWATER

2.1 Introduction

In this Category E-1 are to be found mainly waterproofing grouts based on one of the following two principles:

2.11 Ion Exchange

An ion in the ground is replaced by a different ion contained in the injected solution. This ionic exchange alters the soil's properties, especially its permeability.

For this procedure to work, the ground to be grouted must contain ions with a high exchange capacity, a
condition which obviously does not exist in pure sand. However, this procedure does work with clays. The exchange of an alkaline-earth side-group ion in a clay for an alkaline ion found in the grouting solution, by altering absorptive capacity, increases watertightness and cohesion. Since clayey soils cannot be injected by classic methods (they are not sufficiently permeable), the saline solution must be spread by direct electric current. This electro-consolidation process falls outside the realm of traditional grouting techniques.

In traditional grouting methodology, the ion exchange process is occasionally applicable to sandy soils containing a certain percentage of clay or similar matter. In such cases, some improvement in watertightness can be obtained by injections of mineral or organic solutions. Thus, some cationic solutions have been cited: quaternary ammonium salt (69-11), sodium tetraphosphate (57-06), sodium stearate or palmitate, which may or may not be used in conjunction with an alkaline aluminate (37-19, 39-13, 39-14). In some cases, even sea water may be suitable (57-06).

2.12 Chemical Reaction

In cases where the ground contains high proportions of Ca or Mg salts, direct injection is possible (without a setting agent) and there will form in situ a precipitate or a gel which will waterproof the ground. The simplest example, and one which has enjoyed some applications in Russia for the treatment of loess, would be silicate, which converts to insoluble alkaline silicate upon contact with the ground.

The same principle applies to sodium alginate (conversion to an insoluble calcium alginate gel) (61-26), and also with latex emulsions (precipitation upon contact with water containing Ca and Mg salts) (38-11), or with lead nitrate solutions (39-16).

2.2 Conclusion

These various processes seem to have barely been used, although they would have the advantage of very easy execution. However, they are all too dependent on the ground and thus unreliable. Therefore, no rating has been given for this procedure.
3. CATEGORY E-2: REACTION WITH GROUNDWATER

3.1 Introduction

Some grouts react directly with groundwater, whether it is saline or not. The reaction may be direct, as with silicon chloride (formation of an SiO₂ precipitate) or with isocyanates (formation of polyurea). It may also consist of a modified emulsion or non-aqueous suspension, or of a solution or a suspension in a non-aqueous solvent (both of which would be soluble in water), such as alcohol, acetone or pyridine, which hydrolyze to form a waterproof product on contact with groundwater.

In order to achieve better penetration and avoid any premature reaction during execution, it may be wise to start by putting a water-soluble liquid into the ground (alcohol, ketone, phenols) (41-23), or a product which is not water-soluble (oil) (99-17).

3.2 Products Recommended

Many products operate on one or another of the three principles of direct reaction with groundwater. Thus the following products have been suggested and sometimes used:

3.21 Metallic Salts in Acetone, Alcohol Solutions or Dispersions

Antimony chloride, which gives an antimony oxychloride precipitate (39-15); ferric chloride or sulfate (39-15); silicium or titanium chloride (41-23); bismuth, tin or arsenic salts (39-15), have all been suggested.

3.22 Metallic Alkoxides

In general, metallic alkoxides are solids at ordinary temperatures. They are diluted or dispersed in a non-aqueous solvent: mineral oil, benzene, ketone, carbon tetrachloride. Alkoxides of aluminum, copper or iron are sometimes included (39-18).

3.23 Ethylsilicate

It has been recommended that voids left in oil-bearing strata by the removal of water from these strata be filled with an appropriate solvent which would be soluble
in water and petroleum, alchol, acetone (40-18). It is possible to use setting accelerators which prevent losses of grout in the strata: silicon, zinc, or iron chloride (42-07).

3.24 Silicon or Titanium Tetrachlorides

These substances have been proposed by CHAMBERLAIN (41-23) for use in the oil industry. They give a SiO₂ or TiO₂ gel.

3.25 Cellulose Nitrates or Acetates

These products are dissolved in an organic solvent such as alcohol or acetone (LOOMIS 36-18).

3.26 Natural Resins

Arosinates (KENNEDY 39-15), acaroid resins ("YACCAGUM" or "grass tree gum") in solution in methyl alcohol (LAWTON 44-13) have been suggested.

3.27 Bitumens

Another possibility which has been advocated consists of solutions of bitumen in pyridine, which become diluted with ground water and leave a deposit of bitumen (LIMBURG 40-26).

3.28 Bentonite Suspensions in Oil

Dry bentonite suspended in oil or in fuel can form a gel in the presence of water. This process is used mainly for stopping water ingresses in oil wells (the grout is too viscous to be used for grouting sand). There is a reference to the use of this grout for civil engineering purposes in the DIKAN Dam in Iraq (63-14).

3.29 Polyesters

An inverse emulsion (water in oil) of an unsaturated polyester, modified by an ethylene monomer such as styrene, thickens pronouncedly upon contact with groundwater, stays in place even if subjected to running water, and then polymerizes.

This grout is advocated for terrain which streams with water; it has the advantage of low viscosity, easily
regulated setting time and, above all, it does not wash away, because it thickens instantaneously as soon as it absorbs water (CARON and GRANIER 72-14).

3.210 Polyureas and Polyurethanes

When an isocyanate is made to react on a polyol or a polyether, a polyurethane polymer is formed. The same isocyanate can react directly with water:

\[
R - N = C = O + H_2O \longrightarrow R - NH_2 + CO_2
\]

producing carbon dioxide gas as a polymer is formed. If the formula is gauged correctly, the two reactions take place simultaneously, the carbon dioxide remains occluded in the polymer and a stable foam is formed. Thus, a direct reaction with groundwater is possible with the isocyanate alone, theoretically producing a polyurea foam in situ, but if some parts of the isocyanate were not to enter into contact with groundwater, polymerization would not take place. Thus, CARON and GUITTARD (73-14) advocate the use of a grout combining isocyanate and a small amount of polyol which, upon contact with groundwater, will always form a polyurea polyurethane foam whose proportions will vary according to the amount of water absorbed. There was a major application of this system in Spain at the CANELLES Dam (99-17).

Although its exact composition is not known, the ready-to-use grout of the Japanese firm TAKANEKA DOMUTEN, "TACSS SYSTEM", is a prepolymerized polyurethane which is particularly effective for consolidating and waterproofing ground through which a great deal of water circulates (69-10, 70-03). This grout, slightly diluted with a solvent, sets upon contact with groundwater to form a product which is stable, insoluble, hydrophobic and very light.

The molecule's isocyanate terminal enables it to expand greatly (about 25 times its original size) and to form a foam containing twelve-sided bubbles of carbon dioxide which make the product highly stable (72-05, 72-06, 73-09, 73-11, 73-12, 73-14).

Setting time can be regulated through the use of an amine to shorten the interval, or an acid to prolong it (71-03). This interval can vary from a few seconds to two hours (73-12). It appears that this grout, which is relatively expensive and rather viscous, has not been used to
stabilize or waterproof fine soils (70-03), its special application area being the treatment of rivulets in karstic and similar conditions (66-07, 66-08).

3.3 Rating

These various products have the advantage of being very easy to apply, but because of their extremely limited range of application, no rating has been given.
CHAPTER VII
 CATEGORY F: COMBINED SYSTEMS

1. Introduction

This chapter discusses systems combining some of the preceding principles and examines new products which give the mixtures markedly different properties.

The silicate-bitumen emulsion mixture or the phenoplast resin-bitumen emulsion could have been included in this category as mixtures of Categories A-1 and D-2. However, they have been included in Category D-2 since the major component of each is the bitumen emulsion, the silica gel or the phenoplast resin being added only to help the bitumen emulsion to coagulate. For the same reasons, various other combination systems were examined under the chapter devoted to their principal component.

This chapter is concerned with combinations conferring new properties on the two basic systems, as taken separately. This is the result of a combination of a Category A grout (aqueous solution) with a Category B grout (colloidal systems).

By virtue of their low viscosity, Category A grouts can seep down by simple gravity or be carried horizontally by non-stagnant underground water. An experimental study has been made by CARON (65-03, 70-07), which showed that, some time after injection, the grout has moved down from where it had been injected. As a result of this horizontal or vertical movement, the injected area can actually be some distance from the point intended and calculated. It can even happen that the various injections made through neighboring bore-holes do not meet properly to form a continuous sheet, since their spreading patterns have been different. In this case there will be gaps (windows) in the curtain which render it partially ineffective.

The bentonite-type colloidal grouts (Category B-2) do not give very good performances at the final stage, since the gel's mechanical characteristics are very weak and it risks loosening. However, at the time of preparation they have a certain intrinsic rigidity which prevents them from drifting downward. Thus, it can be advantageous
to combine Categories A and B-2.

2. **A-1 Plus D-2 Combination**

   This grout has been proposed by CARON (72-15) and called SUPERGEL. It includes:

   a) sodium silicate in a much more dilute solution than that used for traditional processes (3.5 to 7% instead of 12 to 35%).

   b) ultra-colloidal bentonite, whose particles are all less than one micron in size.

   c) a polyphosphate or tannin-type peptizer.

   d) a sodium silicate setting reagent which does not produce a flocculating effect on the bentonite. Thus, polyvalent salts must be ruled out (calcium chloride, copper, copper sulfate), as well as highly ionized acids. This reagent should be selected from among the weak organic or inorganic acids (citric, boric or glycolic acid) and the proportion should be about 0.6 to 1.5% by weight.

   This process has enjoyed several applications and its major advantages are: optimal rheological behavior; it is very fluid (3 cP) and has a binghamian rheological character (less than 100 dynes/cm² rigidity). Like silica gels for waterproofing, this grout can be injected into fine soil, but runs no risk of drifting downward because of its intrinsic rigidity. It also tends less toward syneresis. There is no polluting effect because the silicate is used in very low dosages and is completely combined.

3. **A-6 Plus D-2 Combination**

   This is a bentonite suspension combined with an acrylic resin aqueous solution. The PROGIL Company recently recommended such a process for stopping water seepage in mixed terrains (99-07). According to the authors, "the effect of this combination is to make the grout but little viscous while it is moving, but somewhat rigid while it is still. This phenomenon stops the grout from washing and running into large fissures."

   This combination has the same advantages as the preceding procedure, but its relatively high price
seems to have ruled out notable applications.

4. Rating

The rating given in Table 17 is for the most advantageous product in this category, SUPERGEL (A-1 plus D-2 combination).

<table>
<thead>
<tr>
<th>Criterion</th>
<th>Percentage</th>
<th>For Waterproofing</th>
<th>For Consolidation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>30</td>
<td>9</td>
<td>2.7</td>
</tr>
<tr>
<td>2</td>
<td>10</td>
<td>5</td>
<td>0.5</td>
</tr>
<tr>
<td>3</td>
<td>10</td>
<td>9</td>
<td>0.9</td>
</tr>
<tr>
<td>4</td>
<td>10</td>
<td>8</td>
<td>0.8</td>
</tr>
<tr>
<td>5</td>
<td>5</td>
<td>10</td>
<td>0.5</td>
</tr>
<tr>
<td>6</td>
<td>15</td>
<td>10</td>
<td>1.5</td>
</tr>
<tr>
<td>7</td>
<td>20</td>
<td>9</td>
<td>1.8</td>
</tr>
</tbody>
</table>

\[
\text{Total: 8.7}
\]

Table 17. Rating Chart, Supergel
CHAPTER VIII
CONCLUSIONS

1. General Remarks

Several hundred types of chemical grouts were classified and examined for cost, workability, effectiveness, durability, toxicity and environmental impact. These rating categories and their relative importance were given in Table 1. Table 18 is a summary rating for all classified grouts, according to these rating categories.

Some general conclusions have emerged from the examination of these grouts:

1. Most of the grouts proposed and nearly all the grouts actually used are in the aqueous grout categories: A, solutions; B, colloidal suspensions; D, emulsions; F, combinations of A and B. An aqueous grout is obviously less expensive and easier to use than a non-aqueous grout.

2. The Category C and E non-aqueous grouts are therefore limited to very special uses. In Category C, the fluid polyesters, and in Category E, the expanding polyurethanes which react with groundwater, should be noted as the most advantageous.

3. Similarly, some of the aqueous grouts in Categories A, B, D, and F are rarely used as they are suitable only for special purposes. There are:

   - Category A-2, other mineral gels, since these products do nothing that Category A-1 products cannot do, and are more costly.

   - Category A-4, other plant derivatives, since they do nothing that Category A-3 products cannot do, and also because these substances set only in an acid medium.

   - Category A-7, aminoplasts, because these products react only in an acid medium and are therefore useless in any ground containing calcium.
### Table 18. Tentative Evaluation of Grouts

<table>
<thead>
<tr>
<th>CRITERION</th>
<th>MAX score</th>
<th>silicate A1</th>
<th>ligno A3</th>
<th>acryl A5</th>
<th>pheno A6</th>
<th>(AI-A5) A8</th>
<th>organic colloids BI</th>
<th>mineral colloids B2</th>
<th>bituminous emulsions D1</th>
<th>other emulsions D2</th>
<th>(AI-B2) F</th>
</tr>
</thead>
<tbody>
<tr>
<td>1  COST</td>
<td>3</td>
<td>2.4</td>
<td>1.8</td>
<td>0.6</td>
<td>1.5</td>
<td>0.9</td>
<td>1.2</td>
<td>2.4</td>
<td>1.5</td>
<td>0.6</td>
<td>2.7</td>
</tr>
<tr>
<td>2  WORKABILITY</td>
<td>1</td>
<td>0.6</td>
<td>0.7</td>
<td>0.8</td>
<td>0.6</td>
<td>0.8</td>
<td>0.4</td>
<td>0.4</td>
<td>0.7</td>
<td>0.7</td>
<td>0.5</td>
</tr>
<tr>
<td>3  EFFICIENCY</td>
<td>1</td>
<td>0.9</td>
<td>0.9</td>
<td>0.9</td>
<td>0.9</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.9</td>
</tr>
<tr>
<td>4  DURABILITY</td>
<td>1</td>
<td>0.8</td>
<td>0.7</td>
<td>0.9</td>
<td>0.9</td>
<td>0.8</td>
<td>0.3</td>
<td>0.9</td>
<td>1</td>
<td>1</td>
<td>0.8</td>
</tr>
<tr>
<td>5  NON-TOXICITY (at preparation)</td>
<td>0.5</td>
<td>0.5</td>
<td>0</td>
<td>0.15</td>
<td>0.2</td>
<td>0.2</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>6  NON-TOXICITY (once injected)</td>
<td>1.5</td>
<td>1.05</td>
<td>0.9</td>
<td>1.05</td>
<td>1.05</td>
<td>1.05</td>
<td>1</td>
<td>1.5</td>
<td>1.5</td>
<td>1</td>
<td>1.5</td>
</tr>
<tr>
<td>7  NON-DERIVED from PETROLEUM</td>
<td>2</td>
<td>1.6</td>
<td>1.6</td>
<td>0.4</td>
<td>0.8</td>
<td>1</td>
<td>2</td>
<td>2</td>
<td>0</td>
<td>1.6</td>
<td>1.8</td>
</tr>
<tr>
<td><strong>TOTAL SCORE</strong></td>
<td><strong>10</strong></td>
<td><strong>7.85</strong></td>
<td><strong>6.6</strong></td>
<td><strong>4.8</strong></td>
<td><strong>5.85</strong></td>
<td><strong>5.65</strong></td>
<td><strong>5.9</strong></td>
<td><strong>8.2</strong></td>
<td><strong>5.7</strong></td>
<td><strong>5.9</strong></td>
<td><strong>8.7</strong></td>
</tr>
</tbody>
</table>
Table 18. Tentative Evaluation of Grouts (Con't)

<table>
<thead>
<tr>
<th>STRENGTHENING</th>
<th>silicate A1</th>
<th>ligno A3</th>
<th>acryl A5</th>
<th>pheno A6</th>
<th>(Al-A5) A8</th>
<th>other emulsions D2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2.4</td>
<td>1.5</td>
<td>0.3</td>
<td>1.5</td>
<td>0.9</td>
<td>0.6</td>
</tr>
<tr>
<td></td>
<td>0.6</td>
<td>0.7</td>
<td>0.8</td>
<td>0.8</td>
<td>0.8</td>
<td>0.7</td>
</tr>
<tr>
<td></td>
<td>0.7</td>
<td>0.7</td>
<td>0.8</td>
<td>0.9</td>
<td>0.8</td>
<td>0.8</td>
</tr>
<tr>
<td></td>
<td>0.7</td>
<td>0.6</td>
<td>0.9</td>
<td>0.9</td>
<td>0.8</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>0.4</td>
<td>0</td>
<td>0.1</td>
<td>0.2</td>
<td>0.2</td>
<td>0.4</td>
</tr>
<tr>
<td></td>
<td>1.05</td>
<td>0.6</td>
<td>1.05</td>
<td>1.05</td>
<td>1.05</td>
<td>0.8</td>
</tr>
<tr>
<td></td>
<td>1.6</td>
<td>1.6</td>
<td>0.2</td>
<td>0.8</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>7.45</td>
<td>5.7</td>
<td>4.15</td>
<td>6.15</td>
<td>5.55</td>
<td>4.3</td>
</tr>
</tbody>
</table>
-Category B-1 products, organic colloids, for they do not offer any advantages over B-2 products, mineral colloids, (except in special cases), and are more costly.

-Categories C-1, synthetic resins, and C-2, vulcanizable oils, because a grout in emulsion is harder to handle than grouts in solution or colloidal suspension and the results are less predictable.

4. At present the most advantageous products are found in Categories A-1, A-3, A-5, A-6, A-8, B-2 and F.

5. Category A-1 through A-5 and A-6 grouts can be used for waterproofing as well as for consolidation, according to their diluteness.

Category A-3, B-2 and F grouts can be used only for waterproofing. Category A-3 (lignochrome), at maximum concentration, can be used for moderate consolidation. However, at maximum concentration, viscosity exceeds 20 cP.

Category A-8 grout, SIPROGEL, is used specifically for consolidation. This ready-mixed product can also be used for waterproofing, but it would be too expensive.

6. Among all the various grouts, only four categories do not rely on petrochemicals: the inorganic systems, A-1, B-2, F; systems of plant origin, A-3. These will be the most promising in times of oil shortages.

2. Special Findings Regarding the Most Promising Grouts

2.1 Category A-1: Silicates

These grouts are well known as they were the first to be used for chemical grouting. They are thus thoroughly documented both for research and applications, although silicate-base grouts have enjoyed a much greater use in Europe than in the United States.

Silica gels are most useful for both waterproofing and consolidation, and in both cases the quality-price ratio is very good. However, these grouts have three drawbacks:
1. some lack of long-term stability, although this point is still debated;

2. after setting, the gel releases some free sodium, which can be a nuisance;

3. if subjected to stress over a long time, strengths are impaired.

2.2 Category A-3: Lignosulfites

These are of interest because they are derived from almost totally unused residues. Lignosulfite, combined with an alkaline dichromate, converts after a variable interval into a more or less consistent jelly. In some countries, notably the United Kingdom, this grout has competed with silica gels. However, it is limited as it does not give strong mechanical properties, and is used for waterproofing and moderate consolidation. The use of certain additives and careful selection (since it is a by-product, its composition varies from one factory to another) can improve the mechanical properties of the hardened grout. It would seem that lignosulfites offer interesting possibilities for research, as does the question of reducing the proportion of chromium to avoid the problem of toxicity.

There is another product which is of plant origin, does not require chromium for polymerization, and can also be used for consolidation: furfural, whose formulations and possible uses are described at the end of Category A-4. Although some furfural-base mixtures (furfuralanilin) were researched and proposed for consolidation more than twenty years ago (research by Dr. WINTERKORN at PRINCETON University), these studies were not followed up (except for some very special applications in the U.S.S.R.), since these products are so far more costly than resins made from petrochemicals. Thus, although the world produces some 200,000 tons of furfural yearly, not one pound of it is used in chemical grouting.

It is highly probable that furfural and its derivatives (furfurylic alcohol, furfurylidenacetone) have a promising future. Extracted from corncobs, straw, sugar cane bagasse, etc., the supply of this product is renewed each year, and its sources are innumerable. By merely providing for more complete collection of these materials, world production of furfural could be multiplied tenfold.
2.3 **Categories A-5 and A-6: Acrylamide and Phenoplast**

These are two aqueous resins which share the market for the treatment of fine sands. These two grouts are petrochemical derivatives and, all else being equal, are more costly than the two preceding products. They do, however, enjoy appreciable technical advantages. Their initial viscosity is lower, and their viscosity does not evolve prior to setting time. They also enjoy a good long-term performance.

For grouting heterogeneous terrain, treatment is recommended to begin with a silica gel and to be completed by an aqueous resin. If the terrain is definitely heterogeneous with highly permeable voids, it would be technically and economically advisable to plug the voids in advance with an injection of clay-cement or a similar product.

2.4 **Category A-8: Grouts Derived from Category A**

Among the grouts obtained from products in Category A, a comparative study permits the selection of SIPROGEL. This mineral-organic composite, a silica-acrylamide gel, combines some of the advantages and disadvantages of the preceding categories:

- Its high acrylamide content makes it expensive, so it can logically be used only for very special purposes, and is not generally suitable for large-scale applications.

- The major advantage of this composite is that the presence of the acrylamide inhibits the silica gel's tendency to loosen over long stretches of time.

- Although SIPROGEL is perfectly suitable for waterproofing, its high cost limits it to consolidation work.

2.5 **Category B-2: Bentonite Gels**

These substances can be used only for waterproofing, since they acquire only slight rigidity after injection, and there is some risk of long-term loosening.
2.6 Category F: Combined Systems

One of the most promising of these combination grouts is SUPERGEL, a suspension of peptized bentonite combined with sodium silicate and a setting reagent. Like bentonite, SUPERGEL can be used only for waterproofing. But, after a few hours, this grout acquires sufficient shear strength to rule out any risk of loosening. For waterproofing, then, it is one of the products having the best quality-price ratio.
CHAPTER IX
CHRONOLOGICAL BIBLIOGRAPHICAL REFERENCES

00-01  JEZIORSKY
        D.R.P. 39732 (1886)

00-02  M. GARVEY
        Method of stopping seams
        U.S.P. 442,037, December 2, 1890

06-01  N. MEHNER
        Process of solidifying Earthy Ground
        U.S.P. 829,664, August 28, 1906

09-01  E. LEMAIRE and A. DUMONT
        Procédé de creusement de puits de mine ou autres
        excavations en terrains aquifères consistants ou
        inconsistants;
        (Procedure for sinking mine shafts and Other
        Excavation work in solid or Loose Water-Bearing
        Ground).
        F.P. 404,922, July 9, 1909

11-01  A. FRANCOIS
        New or Improved Method for Making Water-Bearing
        Strata Watertight.
        Belgian Patent 8482, 1911

18-01  E. BECKMANN and E. DEHN
        Action of Furfural on Phenols
        Sitzb. Kgl. Preuss. Akad., Wiss. Berlin 1918 -
        1201-21, C.A. 14.642 (1920)

19-01  A. H. KRYNAUW
        Francois & Porter Grouting Process
        30, 1919

19-03  WALLASCH
        G.R.P. 323,665 (1919)

19-04  WALLASCH
        G.R.P. 325,647 (1919)

21-01  JOHN C. SWAN
        Method of Excluding Extraneous Fluids from Wells
        U.S.P. 1,379,657, May 31, 1921
22-01  RONALD VAN AUKEN MILLS
        Process of Excluding Water from Oil and Gas Wells
        U.S.P. 1,421,706, July 4, 1922

22-02  ALBERT FRANCOIS
        Method of Making Fissured Water-bearing strata Watertight
        U.S.P. 1,430,306, Sept. 26, 1922
        F.P. 470,528 (1922)

23-01  J. P. TRICKEY, C. S. MINER and H. J. BROWNLEE

24-01  Sinking Shafts for Coal Mines, Advantages of the Francois Cementation
        The Canadian Engineer Vol. 47, No. 3, p. 163, July 15, 1924

24-02  I. G. FARBERN A.G.
        G.R.P. 522,056 (1924)

25-01  BRITISH CYANIDES CO. LTD. and E. C. ROSSITER
        B.P. 258,950 - July 1, 1925

25-02  BRITISH CYANIDES CO. LTD and E. C. ROSSITER
        B.P. 266,028 - Nov. 5, 1925

27-01  E. BIERMANN
        Ein neues Grunderverfahren
        (A New Soil Technique)
        Deutsche Bauzeitung (German Building Journal)
        Vol. 61, Suppl., Konstruktion und Ausfuhrung
        p. 64 (1927)

27-02  E. BIERMANN
        Versteinung loser Sande als Grundungsverfahren
        (Consolidation of Loose sand as a Foundation method)
        Deutsche Bauzeitung, Vol. 61, Suppl., Konstruktion
        und Ausfuhrung p. 177-183 (1927)

27-03  HUGO JOOSTEN
        Method of Stabilization of Mountain Layers
        G.R.P. 441,622 - March 9, 1927

28-01  B. J. HALL
        Francois Cementation Method
        Coal Age, Vol. 33, p. 106-107, Feb., 1928
28-02  A. MAST
Die chemische Verfestigung von Bodenschichten
(Chemical Consolidation of Soil Layers)
(German Underground Civil Engineering Journal)

28-03  A. MAST
Die praktische Anwendung des chemische Verfesti­
gungsverfahrens von losen Bodenarten bei der Grun­
dung eines Wohnhauses (The practical Application of Chemical Consolidation of Loose Soils in the
Foundation of an Apartment House).
Deutsche Bauzeitung, Vol. 62, Suppl. Konstruktion und Ausfuhrung, p. 82-83 (1928)

28-04  Chemisches Verfestigungsverfahren von Erdschichten
(Chemical Stabilization of Soil Layers)
Beton und Eisen, No. 7, p. 150 (1928)
(Concrete and Steel)

28-05  SCHEIBER, TROTLER and SCHOLZ
Angew. Chem. 41-1305 (1928)

28-06  Fabrique de produits de chimie organique de Laire
(Laire Organic Chemicals Plant)
F.P. 679,321 - Dec. 6, 1928

29-01  K. BACKOFEN
Das chemische Verfestigungsverfahren als Abdich­
tungsverfahren (Chemical Consolidation as a
Waterproofing Method)
Bergtechnik, Vol. 22, p. 162-163 (1929)
(Mountain technology)

29-02  K. BACKOFEN
Grundungen im Moor; Versteinerung Kieselhaltiger
Boden (Foundation in a swamp; Consolidation of
Water-bearing Ground)
Deutsche Tiefbau-Zeitung, Vol. 29, p. 68-70 (1929)

29-03  J. KUHNKE
Neues chemisches Verfahren zur Verfestigung des
Baugrundes beim Erweiterungsbau des Eisenbahnbrücke
über die Spree am Bahnhof Jungfernheide der
berliner Ringbahn (New Chemical Methods of Con­
solidation of Building Foundation in the Construc­
tion of the Extension of the Railroad Bridge Over
the Spree at the Jungfernheide Station of the
Berlin Circular Railroad).
Zentralblatt der Bauverwaltung, Vol. 49, p. 137­
147 (1929)
29-04  SIEMENS  
Neue Hilfsmittel im Grundbau  (New Materials for Use in Foundation Work)  
Siemens-Bauunion Zeitschrift  (Siemens-Buildings Union Journal), No. 1, Jan., 1929

29-05  SIEMENS  
G.R.P. 441,622  (Inhaber: Tiefbau u. Kalteindustrie A.G. and Dr. Ing. H. Joosten)  
Bautechnik, No. 12, p. 198, 1929 (Construction Engineering)

29-06  Francois Grouting Process  
Engineering News-Record, Vol. 102, p. 853, May 30, 1929

29-07  B. J. HALL  
Tunneling a Water-bearing Fault by Cementation  
Engineering News-Record, Vol. 102, p. 874, May 30, 1929

29-08  I. G. FARBEN A.G.  
G.R.P. 550,647 (1929)

30-01  K. BERNHARD  
Versteinerung loser Bodenarten im Grundbau  
(BConsolidation of Loose Soils in Foundation Work)  
Bauingenieur, Vol. 11, p. 202-208, 1930

30-02  K. BUHRIG  
Die chemische Abdichtung und Verfestigung des un­ 
dicht gewordenen Mauerwerks des Toppolczanschacthes der Castellengogrube  
(Chemical Waterproofing and Consolidation of the Pervious Walls of the Toppo­ 
lczan Ditch of the Castellengo Excavation)  
Gluckauf, Vol. 66, p. 607-610, 1930

30-03  INDRA  
Uber die Abdichtung einer wild ausgebrochenen Mineralquelle im Glauberquellengebiet von Franzen­ 
bad  (Re the Waterproofing of a Mineral Spring in the Glauber Spring Area of Franzensbad)  
Internat. Mineralquellen-Zeitung, No. 9, 1930  
(International Mineral Springs Journal)

30-04  H. JAHDE  
Das Verfestigen und Abdichten von Gebirgschichten von Mauerwerk und Beton auf chemischem Wege  
(Chemical Stabilization and Waterproofing of Mountain Layers, Walls and Concrete)  
Kohle und Erz, Vol. 27, p. 685-689, 1930
A. LANG
Erstmalige praktische Grossanwendung des chemischen Versteinungsverfahrens beim Bau der Wassergewinnungsanlage des neuen Wasserwerks der Stadt Düsseldorf "Am Staad" (First Large-scale Application of Chemical Petrification in the Construction of the Dam of the New Waterworks Dept. of the Town of Dusseldorf "Am Staad")
Bauingenieur, Vol. 11, p. 411-416, 432-437, 1930
Das Gas- und Wasserfach, No. 2-4, 1930
Wasser und Gas, Nov. 14 and 18, Dec. 12, 1930

A. LOHMANN
Die Anwendung des chemischen Verfestigungsverfahrens bei der Abdichtung einer Laugendammes und bei Schachtichtigungs Arbeiten auf Dam Lakiwerk Sachsen-Weimer in Unterbreizbach (Rohn) (Application of Chemical Stabilization on the Waterproofing of a Lye Dam and of Shaft Sealing Works on the Kaliwork Sachsen-Weimar Dam in Unterbreizbach)
Kali, Vol. 24, p. 81-85, 1930

W. SICHARDT
Erfahrungen mit der chemischen Bodenverfestigung und Anwendungsmöglichkeiten des Verfahrens (Research in Chemical Soil Consolidation and Possible Applications of the Method)
Bautechnik, Vol. 8, p. 181-186, 1930

German Process Grouts Porous Materials by Chemical Means

Shcutz und Instandsetzung schadhafter Bauwerke (Protection and Repair of Damaged Structures)
Siemens-Bauunion Zeitschrift, 1930

I. G. FARBEN A.G.
F.P. 697,874, June 25, 1930

GEORGE W. CHRISTIANS
Method and Apparatus for Sealing Crevices in Rock Formations or the Like
U.S.P. 1,763,219, June 10, 1930
Les applications du procédé de cimentation François au fonçage de puits, réparation de cuvelage et tracé de galeries en terrain aquifère (Applications of the Francois Cementation process in the Sinking of Wells, Shaft Lining Repairs and Mine Tunneling in Water-Bearing Ground)
Congrès intern. des mines, de la métallurgie et de la géologie appliquée (International Conference on Mining, Metallurgy and Applied Geology)
Liege, 1930

Oberschlesischer Berg und Huttenmannischer Verein Zeitschrift, Vol. 70, p. 415-417, 1931

Der Bau der neuen Rheinbrücke bei Ludwigshafen (Rhein)-Mannheim (Construction of the New Rhine Bridge Near Ludwigshafen)
Bautechnik, No. 38, p. 547, Sept. 4, 1931

Das chemische Verfestigungsverfahren nach Dr. Joosten; Ein wertvolles Hilfsmittel für Gründungen (Method of Chemical Consolidation According to Dr. Joosten: A Valuable Aid in Foundation Work)

Chemische Verfestigung und Abdichtung undichten Mauerwerks und betons (Chemical Consolidation and Waterproofing of Pervious Walls and Concrete)
Bautenschutz, Vol. 2, No. 1, p. 4, Jan. 5, 1931

Grundung der Neubauten für die Augen und Frauen-Klinik der Berliner Universität (Foundations of the New Buildings for the Eye and Women's Clinic of the Berlin University)
Zentralblatt der Bauverwaltung, Vol. 51, p. 588-600, 1931
31-06  HEISE
Das chemische Verfestigungsverfahren von Dr. Joosten (Dr. Joosten's Method of Chemical Consolidation)

31-07  L. JORGENSEN
Solidifying Sand, Gravel and Weak Rock
Western Construction News, p. 591, Nov. 10, 1931

31-08  LABAUME
Die Umbauten am Bahnhof Jannowitzbrücke in Berlin (Reconstruction of the Railway Station at Jannowitzbrücke in Berlin)
Bautechnik, 9, No. 18, p. 255, Apr. 24, 1931
9, No. 19, p. 271, March 1, 1931

31-09  G. MARBACH
Die Bedeutung des chemischen Verfestigungsverfahrens von Joosten für den Bergbau (The Meaning of the Joosten Method of Chemical Consolidation for Mining)
Glückauf, Vol. 67, p. 913-920, 1931

31-10  O. MAST
Chemische Bodenverfestigung und Sicherung von Bauwerken (Chemical Soil Consolidation and Securing of Construction Work)
Deutsche Tiefbau-Zeitung, Vol. 31, p. 54-55, 1931

31-11  W. SCHRODER
Baugrundverfestigung und Instandsetzung einer Eisenbahnbrücke unter Berücksichtigung des schweren Kraftwagenverkehrs (Ground Consolidation and Repair of a Railway Bridge, Taking Heavy Traffic into Consideration)
Bautechnik, Vol. 9, p. 447-450, 1931

31-12  M. J. STAMATIU
Untersuchungen über die Verfestigung und Abdichtung von Gesteinen und Beton auf chemischem Wege (Investigation of the Consolidation and Waterproofing of Stone and Concrete Chemically)
Freiberg in Saar, 1931

31-13  I. G. FARBEN A.G.
U.S.P. 1,791,434 (1931)

31-14  MICHAEL MULLER
Process of Chemically Solidifying Earth
U.S.P. 1,815,876, July 21, 1931
31-15 C. W. CHRISTIANS
Apparatus for Sealing Crevices in Rock Formations or the Like
U.S.P. 1,820,347, August 25, 1931

31-16 CARL ZEMLIN
Process of Solidifying Layers of Ground and Similar Masses
U.S.P. 1,820,722, August 25, 1931

31-17 HUGO JOOSTEN
Process of Solidifying Permeable Rock, Loosely Spread Masses of Building Structures
U.S.P. 1,827,238, October 13, 1931

31-19 JOOSTEN
Verfahren zum Verfestigen von Wasserdurchlässigen Gebirge (Procedure to Consolidate a Pervious Mountain Area)
G.R.P. 516,151, Feb. 2, 1931

31-20 GAYRARD
Belgian Patent 377,785 (1931)

32-01 AUBERTEN M.
Note sur les travaux d'étanchement d'un barrage par la méthode des injections (Note on Dam Waterproofing Work by Grouting Method)
Annales des Ponts et Chausées (Dept. of Bridges and Highways), Vol. 1, No. 3, p. 417-434, May-June, 1932

32-02 H. FEHLMANN
Das chemische Verfestigungsverfahren (Chemical Consolidation Method)
Hoch und Tiefbau, No. 5, 1932

32-03 L. R. JORGENSEN
New Method of Consolidating Foundations

32-04 A. KLEINLOGEL
Das chemische Verfestigungsverfahren nach Dr. Joosten und seine praktische Anwendung im Baugewerbe und Bergbau (The Joosten Method of Chemical Consolidation and its Practical Application in Construction and Mining)
Internationale Bergwirtschaft und Bergtechnik Vol. 25, p. 29-36, 1932
A. KLEINLOGEL
Neue Versuche mit dem Joostenschen chemischen Verfestigungsverfahren (New Research with the Joosten Method of Chemical Consolidation)
Bautenschutz, Vol. 3, p. 49-54, 1932

D. E. MORAN and F. O. DUFOUR
Increasing Bearing power of Clay Soil (Francois Process)

K. A. POHL
Chemical Solidification of Loose Soils
Engineering Progress, Vol. 13, p. 85-88, 1932

K. A. POHL
Emploi de la silicatisation pour la construction dans les terrains meubles; procédé H. Joosten (Use of Silicate Grouts for Construction in Loose Ground; Joosten Process)
Genie Civil, Vol. 100, p. 14-17, 1932

G. WEIDMANN
Die neue Eisenbahnbrücke über den Rhein (The New Railroad Bridge Over the Rhine)
Bauingenieur, No. 1-2, p. 2-10, 1932

G. W. CHRISTIANS
Method and Apparatus for Sealing Crevices in Rock Formations or the Like
U.S.P. 1,858,952, May 17, 1932

KUHN
"Worterbuch des Kolloidchemie" (Dictionary of Colloidal Chemistry)
Dresden-Leipzig, 1932, Steinkopff Ed.

Bataafsche Petroleum Maatschappij
Procédé pour imperméabiliser ou fixer des couches de terre perméables ou mobiles, tels que les sols sableux et autres masses poreuses (Procedure for Waterproofing or Consolidating Permeable or Unstable Ground, Such as Sandy Soils and Other Porous Masses)
F.P. 743,782, Oct. 7, 1932

W. SICHARDT and D. ZEMLIN
Process of Connecting Solidified Soil to Building Structures
U.S.P. 1,846,815, Feb. 23, 1932
C. DIETZ
Kunstliche Sandverkieselung
(Artificial Sand Consolidation)
Zeitschrift fur praktische Geologie, Vol. 41, p. 57-61, 1933

H. JAPP
New Methods of Excavating Quicksand

P. K. JESPERSEN
Grundforstaerkning ved indpresning af kremiske Vaedsker (Soil Consolidation by Chemical Injection).
Byggningsstatistiske Meddelelser, No. 2, 1933

KREB and W. SICHARDT
Die Bedeutung der Grundwasserabsenkung und der chemischen Bodenverfestigung fur die Grundung in
offener Baugrube (The Meaning of Ground Water Lowering and Chemical Soil Consolidation for the
Foundation of an Open Building Excavation)
Bautechnik, Vol. 11, p. 25-29, 1933

H.C. PEFFER, R.L. HARRISSON, SHREVE R.N., ROSTONE
Industrial and Engineering Chemistry, July, 1933

W. SICHARDT
Chemische Abdichtung von Bauwerken und Baugruben
(Chemical Waterproofing in Construction and Excavation) Bautechnik, Vol. 11, p. 455-457, 1933

W. SICHARDT
Chemische Bodenverfestigung und Abdichtung im Tunnelbau (Chemical Consolidation and Waterproofing in Tunnel Construction)
Verein-Deutscher Ingenieure, Zeitschrift, Vol. 77, p. 905, 907, 1933

R.J. VAN LIER
De Chemische brondverkittings Methode van Dr. Joosten (The Joosten Chemical Consolidation Method)
De Ingenieur, Vol. 48, Bouw-en Waterbouwkunde, p. 14-16, 1933

Minnesota Mining and Manufacturing Company
F.P. 756,564, March 22, 1933
33-12 U.S.P. 1,909,786, May 16, 1933
33-13 U.S.P. 1,909,787, May 16, 1933
33-14 U.S.P. 1,909,788, May 16, 1933
33-15 U.S.P. 1,909,789, May 16, 1933
34-01 GOERTZ
Bau der Untergrundbahn Moskau
(The Building of the Moscow subway)
Bautechnik, Vol. 12, No. 33, p. 423-427; No. 35,
p. 449-451, 1934
34-02 O. MAST
Pfeilerverstarkerung mit nachtraglicher Tiefgrund­
ung und der Reichsbahnbrucke uber den Humboldt­
hafen in Berlin (Pile Strengthening and Supple­
mentary Deep Foundation of the Reichs Railroad
Bridge over the Humboldt Harbor in Berlin)
Bauingenieur, Vol. 14, p. 327-331, 1934
34-03 M.J. NEELANDS (Francois Cementation Co.)
Discussion of Paper No. 4905 by Allin and Nacjshen
Proceedings, Institution of Civil Engineers,
Vol. 235, p. 480, 482, May, 1934
34-04 H. WEBER
Das chemische Bodenverfestigungs und Abdichtungs­
verfahren (Chemical Soil Consolidation and Water­
proofing) Siemens Zeitschrift, Vol. 14, p. 383­
388, 1934
34-05 HOFMANN
Ber. 18 - 2765, 1934
34-06 BAKELITE CORP., (F. BITTERICH)
U.S.P. 1,971,476, Aug. 28, 1934
35-01 M. WECKEL
Note sur les grands travaux en Algérie Barrage de
Bou-Hanifa (Note on Major Construction Projects
in Algeria, Bou-Hanifa Dam)
Annales des ponts et chaussées, p. 915, Jan., 1935
35-02 D. DE SIMONE
Procedimenti di impermeabilizzazione e di consoli­
damento chimico di terreni (Chemical Ground Water­
proofing and Consolidation Procedures)
Annali dei Lavori Pubblici (Annals of Public Works)
Vol. 73, p. 443-449, 1935

164
35-03 H.J.B. HARDING
Ground Water Lowering and Chemical Consolidation of Foundations
Concrete and Construction Engineering, Vol. 30, No. 1, p. 3-12, 1935

35-04 A. KARSTEN
Chemische Bodenverfestigung und Abdichtung (Chemical Soil Consolidation and Waterproofing)
Deutsche Bauzeitung, Vol. 69, p. 476-478, 1935

35-05 B.A. RZHANITZIN
How Sands are Transformed into Stones (Russian)
O.N.T.I., P. 37, 1935

35-06 M. STAMOTIVE
Recherches sur l'imperméabilisation et la consolidation du béton, etc... (Research on Cement Waterproofing and Consolidation, etc...)

35-07 Soc. pour l'Industrie chimique a Bale (The Bale Chemical Industry Association)
R.P. 671,724, 1935

35-08 Rhurchemie A.G. (The Rhur Chemical Co.)
F.P. 791,983, July 2, 1935

35-09 I.G. FARBEN A.G.
F.P. 796,389, Oct. 3, 1935

35-10 W. KLEE
Methods and Means for Filling in Concrete Rocks and the Like
U.S.P. 1,987,958, Jan. 15, 1935

35-11 JOHN J. BREBE and SYLVIA M. STOESSER (Assigned to Dow Chemical Co.)
Treatment of Deep Wells
U.S.P. 1,998,756, April 23, 1935

35-12 H.T. KENNEDY and H.C. LAWTON
Method of Plugging Strata in Wells
U.S.P. 2,019,908, Nov. 5, 1935
J.R. JORGENSEN
Method of Grouting by Chemical Means

G.E. BURNETT
Chemical Solidification of Dam Foundations
U.S. Bureau of Reclamation, Library files,
Memo to R.F. Blanks, 0 pp., 1936

I. GUTMAN
The Moscow Subway
Engineering News-Record, Vol. 116, p. 515-521,
April, 1936

H.J.B. HARDING
Chemical Consolidation in the Moscow Subway
Engineering News-Record, Vol. 117, p. 94, July
16, 1936

H.J.B. HARDING
Underpinning and Foundation Work in Loose and Water­
logged Ground by Chemical Consolidation, Ground
Water Lowering and Other Means
Structural Engineer, Vol. 14 (new series), No. 6,
p. 289-294, June, 1936

L. JORGENSEN
Chemical Consolidation in the Moscow Subway
Engineering News-Record, Vol. 117, p. 483, Oct. 1,
1936

K. KIESER
Sicherungsarbeiten am schiefen Turm von Pisa
(Stabilization Work on the Leaning Tower of Pisa)
Schweizerische Bauzeitung (Swiss Building Journal)
Vol. 107, p. 272-273, 1936

KLERLAIN
Construction des accès de la Station "Rue du Tele­
graphe" de la ligne metropolitaine No. 11 de la
place du Chatelet a la porte des Lilas
(Construction of Approaches to the "Rue du Tele­
graphe" Station on the No. 11 Subway Line at the
Place du Chatelet by the Porte des Lilas)
Genie Civil, Vol. 108, No. 2811, p. 597-603,
June 27, 1936

J.S. LEWIS JR.
Methods of Sealing Dam Foundations, Washington
Third World Power Conference, Vol. 1, p. 229, 1936
L.R. JORGENSEN
Process for Grouting Cracks and Contraction Joints
U.S.P. 2,053,562 - Sept. 8, 1936

G. D. RODIO
The Foundation of the Building "La Baloise" in Lugano, Switzerland, Involving Modern Methods in Deep Foundation Technique

ROSSMANN
Der Staudamm des Staubeckens an der Malapane bei Turawa (The Dam of the Basic by Malapane Near Turawa) Bautechnik, Vol. 14, p. 3-6, 28-30, 44-46, 1936; process p. 30

TERZAGHI
Methods for the Artificial Consolidation of the Porous and Fissured Materials

The Basement of a Danish Cathedral Showing How Chemicals Were Forced With Pumps into Soil to Harden it and Prevent the Foundation from Sinking San Francisco Chronicle, March 29, 1936

The Joosten Chemical Consolidation Process
John Mowlen and Co., London, 1936

A.G. LOOMIS et al.
Method of Treating Wells
U.S.P. 2,051,505 - August 18, 1936

H. JOOSTEN
G.R.P. 684,769 - 1936

N.V. DE BATAAFSCHE PETROLEUM MAATSCHAPPIJ
Procédé pour imperméabiliser, rendre étanche ou consolider les terrains et autres masses terreuses ou pierreuses et les constructions (Procedure for Waterproofing or Consolidating Ground and Other Earthy or Rocky Masses and Structures)
F.P. 811,623 - October 6, 1936
37-01  N.V. DE BATAAFSCHE
Consolidating and Waterproofing Earth, Gravel, Concrete, etc.
F.P. 811,623 - April 9, 1937

37-05  JESPersen
Foundations of the Ribe Dom Church
National Tidende, Jan. 31, 1937

37-06  H. JOOSTEN
Chemical Solidification of Loose Soils
The Constructor, August 1937

37-07  H. JOOSTEN
Modern Methods of Impermeabilizing by Injecting Permeable Materials (Neuzeitliche Abdichtungsverfahren mit Einpressen von Dictungsmitteln)
Reprint from Deutsche Wasserwirtschaft, 1937
(Frankh'sche Verlagshandlung, Stuttgart)
(Waterways Experiment Station, Trans. No. 42-13)

37-08  L. JORGENSEN
Solidification of Sand, Gravel, and Granular Material by Chemical Means
Private Bulletin, Berkeley, Calif., 1937

37-09  V.A. KARGHIN
Interaction Between Concentrated Solutions of Sodium Silicate and Calcium Chloride (Russian)
Journal Prikladnoi Chimyl, p. 93-98, Jan., 1937

37-10  L. KRUGER
On the Stability of Chemically Consolidated Soil (Über die Haltbarkeit chemischer Bodenverfestigung)

37-11  J.D. LEWIN
Author's publication, pamphlet, "K.L.M." New York City, 1937

37-12  M. MARTIN
Le barrage de Ghrib (The Ghrib Dam)

37-13  J.E. MEISNER
Grouting to Prevent Leakage Around Earth Dams
Public Works, Vol. 70, 1937

168
37-14 U.S. Corps of Engineers, Conchas District
A Compendium of Grouting, Conchas, NM, 85 pp, 1937

37-15 U.S. Corps of Engineers, St. Paul District
Final Report, Laboratory Tests for Chemical Consolidation of Foundation Materials at Lock and Dam No. 3, Mississippi River, Iowa City Hydraulic Lab., Nov., 1937

37-16 Waterways Experiment Station
New Chemical Grouting Process
Soils Mechanics Bulletin No. 9, p. 8, 1937

37-17 J. MC KAY
Method of Waterproofing Structures
U.S.P. 2,071,758 - Feb. 23, 1937

37-18 JAN VAN HULST
Process for Solidifying Earth
U.S.P. 2,075,244 - March 30, 1937

37-19 G.E. CANNON
Plugging Water Sands by a Soap Precipitate
U.S.P. 2,079,431 - May 4, 1937

37-20 HUGO JOOSTEN
Process for Solidifying Soils
U.S.P. 2,081,541 - May 25, 1937

37-21 JOHN J. GREBE
Method of Preventing Infiltration in Wells
U.S.P. 2,090,626 - August 24, 1937

37-22 A. GUTTMANN
Method of Consolidation, Sealing or Filling Ground, Masonry or the Like
B.P. 484,275 - Sept. 24, 1937, Accepted May 3, 1938

38-01 V. ASKALONOV
Densifying Water-Permeable Soils and Rocks by a Bituminous Emulsion
Stroitel Prom. 16, No. 4, p. 48-53, 1938; C.A., 33, 4758, 1939

38-02 V. ASKALONOV
Impermeabilization of Soil with Bitumen Emulsion
Vovosti Tekhniki, No. 8, p. 35-37, C.A. 32, 6425, 1938
I. GUTMANN
Algerian Rockfill Dam Substructures
Engineering News-Record, Vol. 120, p. 749-751, May 26, 1938

A. KARSTEN
The Joosten Process of Chemical Consolidation and Sealing of Permeable Soil

E. MAAG
The Stabilization and the Impermeabilization of the Foundation Soils (Injections), Lecture given at Fed. Techn. Univ. Zurich, 1938; Waterways Experiment Station, Translation No. 40-7

A. MAST
The Development of the Joosten Process of Soil Consolidation During a Ten-year Period of Practical Application

G. RODIO
Las inyecciones quimicas en los terrenos (Chemical Grouting of Ground)
La Ingenieria, Argentine, No. 764 and 765, June and July 1938

H. WALDECK
Neuzeitliche Abdichtungs- und Sicherungsarbeiten in Schachten (Recent Stabilization and Waterproofing Work in Schachten)
Gluckauf, No. 18, p. 385 and No. 19, p. 409, 1938

Methods Preventing Leakage in Mine Shafts (French)
Le Genie Civil, p. 211, Sept. 9, 1938

CARROLL IRONS
Method of Plugging Porous Strata in Wells
U.S.P. 2,121,036 - June 21, 1938

JAMES G. VAIL
Consolidation of Porous Materials
U.S.P. 2,131,338 - Sept. 27, 1938

A. GUTMANN
Consolidating Ground
G.P. 484,275 - May 3, 1938
39-01 O. BODASCHER
Chemische Verfestigung und Abdichtung in rumaenischen Brunnenbau (Chemical Shoring and Waterproofing in Rumanian Well Construction)
Bautechnik, Vol. 17, No. 10, p. 139-140, March 10, 1939

39-02 The Joosten Chemical Consolidation Process

39-03 J.B. HAYS
Improving Foundation Rock for Dams
Civil Engineering, Vol. 9, No. 5, p. 309-312, May 1939

39-04 F. KOGLER and A. SCHEIDIG
Baugrund und Bauwerk (Building Foundation and Construction)
Wilhelm Ernst and Son, Berlin, 1939

39-05 J.D. LEWIN
Methods of Improving Foundation Rock
ASCE Symposium on Masonry Dams, Paper II-c, Spring Meeting Chattanooga, TN, April 1939

39-06 J.D. LEWIN
Grouting with Chemicals

39-07 J. VAN HULST and G.H. VAN LEEUWEN
Process of Solidifying Soils
U.S.P. 2,158,025 - May 9, 1939

39-08 POLLAK
Modern Plastics - 45 - 1939

39-09 HENKEL and Co.
F.P. 850,814 - Feb. 24, 1939

39-10 HENKEL and Co.
F.P. 851,404 - March 9, 1939

39-12 BAYERISCHE STICKSTOFFWERKE A.G.
F.P. 851,810 - March 18, 1939

39-13 JOHN J. GREBE (Assigned to the Dow Chemical Co.)
Method of Preventing Infiltration in Wells

171
| 39-14 | JOHN J. GREBE (Assigned to the Dow Chemical Co.)  
Method of Preventing Infiltration  
U.S.P. 2,152,308 - March 28, 1939 |
| 39-15 | H.T. KENNEDY  
Process of Shutting Off Water or Other Extraneous Fluid in Oil Wells  
U.S.P. 2,146,480 - Feb. 7, 1939 |
| 39-16 | T.H. DUNN (Assigned to Stanolind Oil and Gas Co.)  
U.S.P. 2,156,219 - April 26, 1939 |
| 39-17 | T.H. DUNN (Assigned to Stanolind Oil and Gas Co.)  
Chemical Plugging Data  
U.S.P. 2,156,220 - April 25, 1939 |
Method of Sealing Off Water and Gas Layers  
U.S.P. 2,169,458 - August 15, 1939 |
| 39-19 | R.J. BALL  
Well-Drilling Fluid  
U.S.P. 2,174,027 - Sept. 26, 1939 |
| 39-20 | T.G. MALMBERG  
Process for Solidifying Permeable Masses  
U.S.P. 2,176,266 - Oct. 17, 1939 |
Canadian Patent 382,960 - July 25, 1939 |
| 39-22 | A.R. NEELANDS  
Grouting Composition  
B.P. 505,211 - May 8, 1939 |
| 39-23 | The Joosten Chemical Solidifications Process  
Mowlen, John and Co., Ltd, Published by authors in London, 28 pp., 1939 |
| 39-24 | A.G. LOOMIS  
Well Treatment Method  
U.S.P. 2,143,990 - Jan. 17, 1939 |
| 39-25 | JAN VAN HULST  
Process for Impermeabilizing Loose Subsoil Layers or the Like  
U.S.P. 2,175,804 - Oct. 10, 1939 |

172
| 40-02 | W.L. DAVIS | Report on Grouting Tests for the Fault Zone in the Left Abutment of the Upper Narrows Dam | U.S. Corps of Engineers, Sacramento District, Feb. 13, 1940 |
| 40-03 | ECKHARDT | The Sealing of Heat Cracks by the Joosten Method | Bautechnik, Vol. 18, No. 5, p. 49-50, Feb. 2, 1940 |
| 40-04 | H.J.B. HARDING and R. GLOSSOP | Chemical Consolidation of Ground in Railway Work | Railway Gazette, Vol. 72, No. 5, p. 147-151, Feb. 2, 1940 |
| 40-05 | J.D. LEWIN | Chemical Consolidation of Ground | Concrete and Construction Engineering (British), Vol. 35, No. 3, p. 135-136, March 1940; see also Engineering News-Record, p. 221-222, Aug. 17, 1939 |
| 40-06 | Prof. PALLMANN and H. DENEL | Le problème de l'étanchement des sables par injection de systèmes colloidaux (Waterproofing Sand by Grouting with Colloidal Systems) | Agriculturchemisches Institut der E.T.H. Zurich July-August 1940 |
| 40-07 | H.WEBER | Das chemische Bodenverfestigung und Abdichtungsverfahren (Method of Chemical Consolidation and Waterproofing) | Siemens Zeitschrift, Vol. 20, No. 1, p. 17-20, Jan.-Feb., 1940 |
| 40-09 | STAGER | | Kunst. Techn. 10, 65, 1940 |
| 40-10 | L'impregnation (Injection) | | F.P. 865,407 - Jan. 24, 1940 |
L'impregnation (Injection)
F.P. 865,408 - Jan. 24, 1940

JAN VAN HULST
Process of Fixing and Impermeabilizing Soil Masses
U.S.P. 2,190,003 - Feb. 13, 1940

G.H. VAN LEEUWEN
Process of Impermeabilizing, Tightening or Consolidating Grounds and Other Earthy and Stony Masses and Structures
U.S.P. 2,197,843 - April 23, 1940

W.B. LERCH, C.H. MATHIS and E.J. GATCHELL (Assigned to Philips Petroleum Co.)
Method of Sealing of Fixing Casing Tubes in Wells
U.S.P. 2,198,120 - April 23, 1940

F.A. BENT, A.G. LOOMIS and H.C. LAWTON (Assigned to Shell Dev. Co.)
U.S.P. 2,200,710 - May 14, 1940

H.C. LAWTON and A.G. LOOMIS (Assigned to Shell Dev. Co.)
Method of Treating Oil and Gas Wells
U.S.P. 2,294,233 - June 11, 1940

H.C. LAWTON (Assigned to Shell Dev. Co.)
Method of Sealing Off Porous Formations
U.S.P. 2,208,766 - July 23, 1940

H.T. BYCK, J.W. FREELAND and H.C. LAWTON (Assigned to Shell Dev. Co.)
Method of Treating Oil and Gas Wells
U.S.P. 2,211,688 - Aug. 13, 1940

W.B. LERCH, T.M. WHITE and E.J. GATCHELL (Assigned to Philips Petroleum Co.)
Process for Plugging Formations
U.S.P. 2,214,423 - Sept. 10, 1940

C.R. IRONS (Assigned to the Dow Chemical Co.)
Treatment of Wells
U.S.P. 2,219,319 - Oct. 29, 1940

ORIE N. MANESS (Assigned to the Dow Chemical Co.)
Method of Cementing Wells
U.S.P. 2,219,325 - Oct. 29, 1940
40-26 H. LIMBURG (Assigned to Shell Dev. Co.)
Process for Sealing Water Bearing Strata
U.S.P. 2,223,789 - Dec. 3, 1940

40-27 S.P. HART (Assigned to Texas Co.)
Treatment of Oil Wells
U.S.P. 2,224,120 - Dec. 3, 1940

40-28 U. KELTENIMIND
Process for Chemical Solidification of Loose or
Porous Masses, in Particular Sandy Ground
B.P. 517,088 - 1940

40-29 W. R. MORGAN et al.
Mechanism of the Hardening of Clay-Sodium Silicate
Mixtures
Journal American Ceramic Society, Vol. 23, No. 6,
p. 170, March 1940

40-30 JAN VAN HULST
Process for Solidifying Earth
U.S.P. No. 2,201,459 - May 21, 1940

40-31 C.F. PRUTTON
Method of Lining Well Bores
U.S.P. 2,236,836 - April 1, 1941

41-02 H.N. FISK
Chemical Hardening of Soil. Annotated Bibliography
on Methods of Inhibiting the Flow of Underground
Water, 1941

41-03 C.F. KOLLBRUNNER and C. BLATTER
Injektionen Verfestigung und Abdichtung von durch­
lassigen Boden, fein zerklufteten Gesteinen, poro­
sem Mauerwerk, Beton, etc (Use of Injection in
Consolidation and Waterproofing of Pervious Soil,
Finely Fissured Rock, Porous Walls, Concrete, etc.)
Privat Gesellschaft fur Bodenforschung und Erdbau­
mechanik (Translated by H.A. WINTERKORN)
Zurich Bericht, No. 4, p. 52, June 1941

41-04 J.J. POLIVKA
Grouting With Chemicals
Engineering News-Record, Vol. 127, p. 83, Oct. 23,
1941

41-05 C.M. RIEDEL
Chemical Joint Sealing and Soil Solidification
H. SEEGER
Hoechstbelastetefundamente auf Sandboden
Deutsche Bauzeitung (German Construction Journal)
Vol. 75, No. 13, p. 231-237, March 26, 1941

Solving a Tricky Dewatering Problem

S.N. FARMER
Chem. Age, 45 23-5, 1941

T.S. HODGINS et al.
Ind. Eng. Chem., 33, 769-779, 1941; C.A. 35, 75773, 1941

CHARLES LANGER
Process of Stanching and Consolidating Porous Masses
U.S.P. 2,227,653 - Jan. 7, 1941

H.T. KENNEDY and A.J. TEPLITZ (Assigned to Gulf Res. and Dev. Co.)
U.S.P. 2,229,177 - Jan 21, 1941

CHARLES S. ACKLEY
Method of Solidifying Porous Earth Materials
U.S.P. 2,232,898 - Feb. 25, 1941

CHARLES S. ACKLEY
Method of Rendering Earth Materials Solid
U.S.P. 2,235,695 - March 18, 1941

W.B. LERCH, C.H. MATHIS and E.J. GATCHELL
(Assigned to Philips Petroleum Co.)
Process for Plugging Formations
U.S.P. 2,236,147 - March 25, 1941

L.C. CHAMBERLAIN and H.A. ROBINSON
(Assigned to the Dow Chemical Co.)
Treatment of Earth Formation
U.S.P. 2,238,930 - April 22, 1941

C.H. MATHIS (Assigned to Philips Petroleum Co.)
Product and Process for Plugging Formations
U.S.P. 2,252,271 - August 12, 1941

L.S. WERTZ
U.S.P. 2,254,252 - Sept. 2, 1941

176
41-18  J.G. MEILER  
Furfuryl Alcohol Resin  
U.S.P. 2,243,481 - May, 1941

41-19  J. VAN DEN BERGE and F. DIJKSTRA (to Shell Dev. Co.)  
Method of Ground Fixation With Bitumens  
U.S.P. 2,258,829 - 1941

41-20  F.A. BENT and A.G. LOOMIS (Assigned to Shell Dev. Co.)  
U.S.P. 2,259,875 - October 21, 1941

41-21  F.A. BENT and A.G. LOOMIS (to Shell Dev. Co.)  
U.S.P. 2,265,962 - Dec. 9, 1941

41-22  NORRIS JOHNSTON (Assigned to Socony Vacuum Oil Co.)  
U.S.P. 2,267,683 - Dec. 23, 1941

41-23  L.C. CHAMBERLAIN (Assigned to the Dow Chemical Co.)  
Treatment of Wells Producing Mineral Fluid  
U.S.P. 2,267,855 - Dec. 30, 1941

41-24  Soc. pour l'industrie chimique à Bâle  
(The Bale Chemical Industry Association)  
F.P. 872,766 - May 29, 1941

41-25  I.G. FARBEN A.G.  
F.P. 873,856 - 1941

41-26  CLEMENT L. and RIVIERE C.  
Composition à base de résines synthétiques  
(Synthetic Resin-Base Composition)  
F.P. 874,248 - March 24, 1941

41-27  Studies on Silicic Acid Gels  

41-28  J. VAN DEN BERGE and F. DIJKSTRA  
Method of Ground Fixation with Bitumens  
U.S.P. 2,258,829 - Oct. 14, 1941

42-01  P. DEVAUX  
La pétirifiation du sol (Ground petrification)  
La Nature, No. 3078, p. 44-48, 1942

42-02  Chemical Solidification of Foundation Material,  
Recl. Laboratory Report No. P 26, Jan 16, 1942

42-03  Chemical Solidification of Foundation for Footings,  
New High School Building, Boulder City, NV, U.S.  

177
Investigation of Soil Stabilization with Vinsol Resin Tech. Memorandum No. 196-1, Waterways Exp. Station, Nov. 1942

Y. HACHIHAMA and M. IMOTO
Phenol Furfural Resins
J. Soc. Chem. Ind. Japan 46, 808-10, 1942

H.A. REIMERS
Method of Stopping Leaks
U.S.P. 2,302,913 - Nov. 24, 1942

H.T. KENNEDY (Assigned to Gulf Res. and Dev. Co.)
Sealing Porous Formations

C. IRONS and S.M. STOESSER (to the Dow Chem. Co.)
Method of Treating Earth and Rock Formations
U.S.P. 2,274,297 - Feb. 24, 1942

J.B. STONE and A.J. TEPLITZ
Earth Consolidation
U.S.P. 2,281,810 - May 5, 1942

JOHN J. GREBE (Assigned to Dow Chemical Co.)
Treatment of Wells
U.S.P. 2,294,294 - August 25, 1942

C.R. IRONS (Assigned to the Dow Chemical Co.)
U.S.P. 2,298,129 - Oct. 6, 1942

G.H. VAN LEEUWEN
U.S.P. 2,300,325 - Oct. 27, 1942

I.G. FARBEREN A.G.
F.P. 879,237 - Feb. 11, 1942

SOC. BELGE DE L'AZOTE
F.P. 921,565 - 1942

Soil Stabilization for Undisturbed Sampling by Chemical Grouting
University of Maine, Doc. 1533, p. 32, 1942

Soil Petrification with Sodium Silicate and Calcium Chloride
The Denver Fire Clay Co., revised Denver, CO, 1943

D.G. HEFLEY and P.H. CARDWELL
Use of Plastics in Water Control
The Petroleum Engineer, p. 51, Dec. 1943
R.R. MINIKIN
Artificial Consolidation of Sub-Foundations
Civil Engineer (British), Vol. 38, No. 444, p. 118-121, June 1943

C.M. RIEDEL
The Joosten Chemical Soil Solidification Process
Improvement Bulletin, June 4, 1943

Chemical and Other Grout Tests on the John Martin Foundation Sandstone

C.H. MATHIS and CARL RAMPACEK (to Philips Petroleum)

GUTTMANN A. and J. MOWLEM
Treatment of Sandstone for Consolidating Sealing or Strengthening the Same
B.P. 553,310 - May 17, 1943

G.H. VAN LEEUWEN (Assigned to Shell Dev. Co.)
U.S.P. 2,319,020 - May 11, 1943

F.D. SULLIVAN
Grouting Means and Process
U.S.P. 2,320,954 - June 1, 1943

C.H. MATHIS and CARL RAMPACEK (to Philips Petroleum)
U.S.P. 2,321,761 - June 15, 1943

ABRAHAM B. MILLER (Assigned to Hercules Powder Co.)
Soil Stabilization
U.S.P. 2,323,928 - July 13, 1943

A.B. MILLER (Assigned to Hercules Powder Co.)
Stabilization of Soils
U.S.P. 2,323,929 - July 13, 1943

G.H. VAN LEEUWEN
Process of Impermeabilizing, Tightening or Consolidating Grounds and Other Earthy and Stony Masses and Structures

H.A. REIMERS (Assigned to the Dow Chemical Co.)
U.S.P. 2,330,145 - Sept. 21, 1943
MILTON WILLIAMS (Assigned to Standard Oil Dev. Co.)
Plugging of Water Sands

BATA A.S.
F.P. 897,513 - August 25, 1943

SINNOVA
F.P. 906,953 - Jan. 27, 1943

M. LANDECKER
F.P. 899,299 - Oct. 29, 1943

G.W. MC ALPIN, H.F. WINTERKORN and R.C. MAINFORT
A Laboratory Study of the Soil Stabilization Effectiveness of a Complex Salt of Abietic Acid

A.G. AREND
Development in Solidifying Loose Soils
Civil Engineer, London, Vol. 39, No. 451, p. 16-17, Jan. 1944

G. PIETTE
Improved Soil Stabilization
Engineering Journal, Vol. 27, p. 413-416, July 1944

M. POLIVKA
Soil Solidification by Means of Chemical Injection
M.S. Thesis, University of California, 1944

Consolidating Loose Soils, Highway - Silicates
Roads & Road Const., Vol. 22, No. 256, p. 103-104, 1944

L.B. OLMSTEAD and L.W. KLIPP
Chemical Stabilization of Soils for Military Uses

W.S. PENN
Brit. Plastics, 16, 286-92, 1944; C.A. 38, 6006, 1944

K.L. VONDER AHE and H.C. ZWEIFEL (to Richfield Oil)
Production of Petroleum

S.E. BUCKLEY and G.G. WRIGHTSMAN (to Standard Oil)
Method for Selectively Plugging Water Sands
44-10  W.B. LERCH, C.H. MATHIS and E.J. GATCHELL  
(Assigned to Philips Petroleum Co.)  
U.S.P. 2,345,611 - April 4, 1944

44-11  E.F. FIEDLER, ADAMS and G.D. HOLMBERG  
Production of Resins from Furan Derivatives  
U.S.P. 2,345,966 - April 4, 1944

44-13  H.C. LAWTON  (Assigned to Shell Dev. Co.)  
Method of Sealing Off Porous Formations  
U.S.P. 2,348,484 - May 9, 1944

44-14  W.B. LERCH, C.H. MATHIS and E.J. GATCHELL  
(Assigned to Philips Petroleum Co.)  
U.S.P. 2,349,181 - May 16, 1944

44-15  ABRAHAM B. MILLER  (Hazel E. Miller, administratrix)  
Stabilization of Soil  
U.S.P. 2,357,124 - August 29, 1944

44-17  K.H. ANDERSEN  (Assigned to Case, Pomeroy and Co.)  
U.S.P. 2,365,039 - Dec. 12, 1944

44-18  M.C. LEVERETT and G.G. WRIGHTSMAN  
(Assigned to Standard Oil Dev. Co.)  
U.S.P. 2,366,036 - Dec. 26, 1944

44-19  Deutsche Hydrierwerke A.G.  
F.P. 903,934 - May 3, 1944

44-20  Abrasive Bodies, Registered Aug. 2, 1941  
B.P. 561,736 - June 2, 1944

44-21  Abrasive Articles, Registered Oct. 23, 1941  
B.P. 562,715 - July 13, 1944

44-22  V.A. ENDERSBY  
Method of Preventing Landslides  
U.S.P. 2,348,458 - May 9, 1944

44-23  M.T. HARVEY  
U.S.P. 2,343,972 - March 14, 1944

45-01  R.C. MAINFORT  
A Laboratory Study of the Effectiveness of Various  
Chemicals as Soil Stabilizing Agents  
U.S. Civil Aero. Admin., Tech. Dev. Note No. 40  
Oct. 1945
45-02  C.M. RIEDEL
Chemical Soil Solidification and Chemical Sealing
Journal, American Water Works Assn., Vol. 37,
p. 849-862, Sept. 1945

45-03  Chemical Injections Solidify Soil to Stop Foundation Settlement
Construction Methods, Vol. 27, No. 12, p. 78-79,
156-158, 160-162, Dec. 1945

45-04  H.F. WINTERKORN, R.G. FEHRMAN and G.W. MC ALPIN
Waterproofing Cohesive Soils by Resinous Treatment
Soil Science Society of America, Proceedings,
Vol. 10, p. 458-460, 1945

45-05  H.F. WINTERKORN
A Laboratory Study of the Effectiveness of Various
Chemicals as Soil Stabilizing Agents, U.S. Dept.
of Commerce, C.A.A., Tech. Dev., Note No. 40,
Oct. 1945

45-06  E.A. REINECK
U.S.P. 2,367,312 - 1945

45-07  A.B. MILLER (Assigned to Hercules Powder Co.)
Stabilizing Soil
U.S.P. 2,369,682 - Feb. 20, 1945

45-08  T.K. MILES
Process for Ground Fixation
U.S.P. No. 2,378,235 - June 12, 1945

45-09  A.B. MILLER
Soil Stabilization
U.S.P. 2,377,639 - June 5, 1945

45-12  Imperial Chemical Industries
Colles et résines synthétiques (Glues and Synthetic Resins)
F.P. 919,112 - Dec. 18, 1945

45-13  J.F.T. BLOTT (B.P. applied on June 18, 1943)
B.P. 569,489 - May 25, 1945

46-02  W.D. LAWS and J.B. PAGE
Silicate of Soda as a Soil Stabilization Agent
Highway Research Board, Bull. No. 1, May 1946,
J. of M. Soc. of Agronomy, p. 95-97, Vol. 38
| 46-03 | J.H. BAXENDALE, M.G. EVANS and G.S. PARK  
C.A. 41, 640c, 1947 |
| 46-04 | A.P. DUNLOP and F.N. PETERS, JR.  
Furan Resins, Colloid Chemistry, 6, 1048-62, 1946;  
C.A. 40, 23512, 1946 |
| 46-05 | DELMAR H. LARSEN  
Process of Compacting or Sealing Formations  
U.S.P. 2,393,173 - Jan. 15, 1946 |
| 46-06 | H.T. KENNEDY and P.L. BASSETT (to Res. & Dev. Co.)  
U.S.P. 2,411,793 - Nov. 26, 1946 |
| 46-07 | ANDRESEN  
Method of Oil Recovery  
U.S.P. 2,402,588 - June 25, 1946 |
| 46-08 | C.M. RIEDEL  
The Joosten Chemical Soil Solidification Process  
Published by the author, Chicago, 1946 |
| 46-09 | H.F. WINTERKORN  
Principles and Practice of Soil Stabilization from  
Technological Applications of Colloid Chemistry,  
Theoretical and Applied  
Vol. VI, Jerome Alexander, Ed., Chemical Catalog,  
New York, 1946 |
| 46-10 | Dow Chemical Co.  
Chemical Soil Solidification Accomplished with  
Calcium Chloride, Dowflake, Jan. 1946 |
| 46-11 | B.W. NORDLANDER  
U.S.P. 2,399,055 - April 23, 1946 |
| 47-01 | U.S. Waterways Experiment Station  
Investigation of Soil Stabilization with Vinsol  
Resins, Vicksburg, MS, Tech. Memo. No. 196-1,  
Nov., 1947 |
| 47-02 | F. SCHUTZ  
Nya metoder att oka stabilitet och tathet hos jord  
(New Methods of Increasing the Stability and Tightness of Earth)  
Svenska Vagforeningens Tidskrift, No. 3, p. 72-82,  
1947 |
| 47-03 | B.C. WILKAS |
|       | Report on Chemical Solidification of Warehouse |
|       | Foundation, Bur. of Recl. Files, Davis Dam Proj., |
|       | Oct. 2, 1947 |
| 47-04 | H.F. WINTERKORN |
|       | A Laboratory Study of Soil Stabilizing Effectiveness of Artificial Resins with Special Emphasis on the Anilin-Furfural Resins |
|       | U.S. Dept. of Commerce; C.A.A. Washington, 1947 |
| 47-05 | R.D. TERZAGHI |
|       | Report on the Significant Properties of Silica Gels |
|       | Personal communication, 1947 |
| 47-06 | R.W. MONCRIEFF |
|       | Paint Manufacture, 17, 149-153, 1947 |
| 47-07 | R.H. SMITH and A.C. POLK JR. |
| 47-09 | H.R. REYNOLDS and P. PROTOPAPADAKIS |
|       | Practical Problems in Soil Mechanics, Part XIV, Artificial Cementation and Ground Water Lowering |
| 47-10 | S.S. KISTLER |
|       | Halohydrin Reacted Aromatic Amine Polymer |
|       | U.S.P. 2,416,262 - Feb. 18, 1947 |
| 47-11 | G.E. LITTLE & K.W. PEPPER |
| 47-12 | P.H. CARDWELL |
| 47-13 | W.H. ADAMS |
|       | U.S.P. 2,416,038 - Feb. 18, 1947 |
| 47-14 | H.I. HERSH |
|       | U.S.P. 2,432,890 - Dec. 16, 1947 |
J.R. BAPTISTA JR.  
Injeccoes quimicas nos terrenos (Chemical Injection in Soils) Ordem dos Engenheiros Revista, Vol. 6, No. 59, p. 553-565, Nov. 1948

E. ISCHY  
Lac Noir Dam, Stanching and Reinforcing Third Congress on Large Dams, Ques. No. 10, R37, Stockholm, 1948; also Congress of Soil Mechanics, Rotterdam, June 1948

A. MAYER  
The Most Recent Precautions to Avoid the Formations of Pipings, Third Congress on Large Dams, Ques. No. 10, R22, Stockholm, 1948

Ground Under Building Stabilized by Grouting Contractors and Engineers Monthly, Feb. 1948

J.J. POLIVKA  

KARL TERZAGHI  
The Most Recent Precautions to Avoid the Formation of Pipings, Third Congress on Large Dams, Ques. No. 10, Stockholm, 1948

M. FOURNIER  

H.F. MULLER and I. MULLER  
Kunststoffe 38, 221-6, 1948; C.A., 43, 1603c, 1949

S.R. FINN and L.R. ROGERS  

S.G. COHEN and D.B. SPARROW  

Final Report, Phase I, Soil Solidification Project. Massachusetts Institute of Technology (MIT), 1948

BOELTER, L.M.K. and Staff  
Chemical Solidification with Silicates; Report to the War Dept. by the Engineering Soil Solidification Research Group, 1948
R.M. HODGSON
Process for the Hardening of Soil and the Like
No. 2,437,387 - March 9, 1948

GARY R. WAGNER (Assigned to Philips Petroleum Co.)
Process for Plugging Wells
U.S.P. 2,439,833 - April 20, 1948

E. FARBER
Conversion of Furfuryl Alcohol
U.S.P. 2,445,137 - July 13, 1948

E. ROHRMANN
Aldehyde Derivatives of 2-Amino Alkanes
U.S.P. 2,455,193 - Nov. 30, 1948

S.S. KURTZ and SWEELY J.S.
Phenol-Aldhyde Sealing Agent and Method of Making the Same

THOMAS JAMES BURN ARTHUS (Applied in 1946)
B.P. 607,104 - Aug. 25, 1948

C.F. KOLLBRUNNER

Etanchement et stabilisation du terrain encaissant un souterrain de chemin de fer métropolitain de Paris par injections systematiques sous pression de produits chimiques en présence d'une nappe phénê­liqueuse (Waterproofing and Stabilization of Ground Surrounding a Paris Subway Line by Systematic Injections of Chemicals Under Pressure in the Presence of a Phenol Solution), Travaux Communication No. IX C/13 au Congres de mécanique des sols à Rotterdam, (Congress on Soil Mechanics, Rotterdam), 1948

Solid Water-Repellency Composition

T. BRISTOW

186
49-02  K. E. CLARE
L'imperméabilisation des sols par matériaux résineux (Ground Impermeabilization with Resinous Materials), London, J. Soc. Chem. Ind., 68, 69-76

49-03  A. DEBERCQ
La silicatisation des terrains (Ground Silicatization), Journal du bâtiment et des travaux publics, Zurich (Building and Public Works Journal, Zurich), L'entreprise No. 10, March 5, 1949

49-04  J. P. ELSTON
Bureau of Recl., Field Trip Report No. 745, Nov. 19, 1949

49-05  H. JAHDE
Neue Erfahrungen auf dem Gebiete der Verfestigung und Abdichtung des Undergrundes (New Research into the Field of Underground Consolidation and Waterproofing), Bautechnik-Archiv, No. 5, p. 3-24, 1949

49-06  J. W. JOHNSON and C. M. RIEDEL
Water Stopped in Alpha Slope by Chemical Sand Solidification, Coal Age, p. 78, July 1949

49-07  C. M. RIEDEL
Latest Developments in Soil Solidification, Midwest Engineer, Vol. 1, No. 6, p. 6-8, Feb. 6, 1949

49-08  R. E. WRIGHT

49-09  H. F. WINTERKORN

49-10  Chemical Consolidation of Soils

49-11  Chemical Treatment Cures Sick Tunnel
Construction Methods and Equipment, Vol. 31, p. 66, Sept. 1949

187
Foundation Grouting, Engineering Manual, Civil Works Construction, U.S. Corps of Engineers, Chapter 1, April, 1949

Rock Out of Sand
Calcium Chloride Association News, Vol. 15, No. 4, p. 8-9, 1949

Solidification of Running Sand, Silicate P's and Q's, Vol. 29, No. 1, p. 2, 1949; (This article describes the same job as reference 48-05, Injected Fluid Stops Running Sand)

J.F.T. BLOTT
Composition Suitable for the Construction of Roads, Paths, Floors, Airdrome Runways, and the Like
U.S.P. 2,473,326 - June 14, 1949

P.H. CARDWELL (Assigned to the Dow Chemical Co.)
Forming Sealing Deposits in Wells
U.S.P. 2,485,527 - Oct. 18, 1949

M.C. DAILEY (Assigned to U.S. Gypsum Co.)
U.S.P. 2,492,212 - Dec. 27, 1949

L.W. FARKAS and M.M. SZWERE
Acid Resisting Cement and Method of Making
U.S.P. 2,492,790 - Dec. 27, 1949

P.L. MC WHORTER, JR.
U.S.P. 2,471,438 - May 31, 1949

A. DEBECQ
Le durcissement et la stabilisation des terrains par silicatisation (The Hardening and Stabilization of Ground by Silicate Grouting)
L'industrie chimique, No. 394, p. 122, May 1950

R. GLOSSOP
Classification of Geotechnical Processes
Geotechnique, Vol. 2, No. 1, p. 3-12, 1950

R.H. HENLEY, H.J. SIELAND and E.R. HOLDEN
Beach Soil Stabilization - Aniline-Furfural Method

KEIL
Funfundzwanzig Jahren Joosten-Verfahren im Bergbau (25th Anniversary of the Joosten Technique in Mining)
Gluckauf, No. 31-32, 1950
50-06  S.R. MAYO  
Chemical Soil Stabilization Doubles Production on Pneumatic Sewer Tunneling Job, Construction Equipment, June 1950

50-07  W. SICHERDT  
Erfahrungen mit der chemischen Boden Verfestigung und Anwendungsmöglichkeiten des Verfahrens (Study of Chemical Soil Consolidation and Possible Application of the Method), Bautechnik, Berlin, W. Germany, p. 181-186, March 18, 1950

50-08  A.W. SIMONDS, F.H. LIPPOLD and R.E. KEIM  
Treatment of Foundations for Large Dams by Grouting Methods, Proceedings, ASCE, Feb. 1950

50-09  V.B. SMITH  

50-10  SPATNY  
Kritisches zur chemischen Bodenverfestigung (Critical Evaluation of Chemical Soil Consolidation) Neue Bauwelt, No. 21, April 10, 1950


50-13  Nouvelle méthode de stabilisation des sols par l'emploi de l'acrylate de Ca (New Method of Ground Stabilization Using Calcium Acrylate) Roads and Streets, 93, 1950

50-14  J.F. MC DONALD  

50-15  O.R. SWEENEY and L.K. ARNOLD  

50-16  R.A. BARKHUFF, JR.  
U.S.P. 2,513,614 - July 4, 1950
50-17  J.C. SEAVER, A.F. SHEPARD and R.W. LESS  
(Assigned to Durez Plastics and Chem., Inc.)  
U.S.P. 2,527,581 - 1950  

50-19  ASKALANOV et al.  
Application of Silicate Treatment to Loose Soils  
Stroitel Prom., Vol. 28, No. 4, p. 10-12, 1950  

50-20  R.C. MERRIL and R.W. SPENCER  

50-21  W.G. SIMONS  
U.S.P. 2,518,388 - August 8, 1950  

51-01  Applied Research, Chrome-Lignin Process and Soil  
Research, Ithaca, NY, 1946-51  

51-02  H. JAHDE  
Baugrundverfestigung und Abdichtung durch chemische  
Verfahren (Chemical Consolidation and Waterproof­
ing of Foundations), Planen une Bauen, No. 24, 1951  

51-03  T.W. LAMBE  
Stabilization of Soils With Calcium Acrylate  
Journal, Boston Society of Civil Engineers, Vol. 38,  
No. 2, p. 127-154, April 1951  

51-04  R.C. MAINFORT  
Summary Report on Soil Stabilization by Use of  
Chemical Admixtures, U.S. Civil Aeronautics Admin.,  
See also Abstract in Roads and Engineering Const.,  
Vol. 89, No. 10, p. 112, 114, 137-140, 142-143,  
Oct. 1951  

51-06  P.F. ZACCHEO  
The Stabilization and Impermeabilization of Soils  
by the Injection of Calcium Acrylate  
M.S. Thesis, MIT, 1951, (Bibliography: p. 91-93)  

51-07  C.M. RIEDEL  
Chemical Stops Cofferdam Leaks, Civil Engineering,  

51-08  L.E. SMYTHE  
J. Amer. Chem. Soc., Vol. 73, p. 2735-8, 1951

190
51-09  Bibliography of Pressure Grouting, 1891-1951
Technical Bibliography No. 214, U.S. Dept of the
Interior, Bureau of Recl., Design and Const. Div.,
Technical Library, Denver, CO

51-10  H.F. WINTERKORN
A Fundamental Approach to the Stabilization of
Cohesive Soils, Highway Research Board, Proc., 28,
415-22, 1948, C.A. 45, 5900f, 1951

51-11  G.G. WRIGHTSMAN (Assigned to Standard Oil Dev. Co.)
U.S.P. 2,556,863 - June 12, 1951

51-12  A.P. DUNLOP and P.R. STOUT
U.S.P. 2,570,027 - Oct. 2, 1951

51-13  B. THOMAS
U.S.P. 2,571,994 - Oct. 23, 1951

51-14  NOMA T. and I. SAKURARA
Japan Patent 3097 - 1951

51-15  P.H. CARDWELL
Treatment of Earth Formations Penetrated by a
Deep Well Bore
U.S.P. 2,541,688 - Feb. 13, 1951

51-16  K. KEIL
Ingeniergeologie und Geoteknick
W. Knapp Halle, p. 995-1014, 1951

51-17  WEIL and HAUSER
Formation et structure de gel de silice (Formation
and Structure of Silica Gel)

51-18  E.C. GERSHOY and C. MUELLER
Soil Stabilization Speeds Tower Footing
Electrical World, p. 66, June 15, 1951

52-01  S.J. BUCHANAN
Military Application of Soil Stabilization
Proceedings of the Conference on Soil Stabilization
MIT, p. 295, 1952

52-02  R.C. MAINFORT
Discussion, Chemical Soils Solidification Work
in Construction and Emergencies
Proceedings of the Conference on Soil Stabilization
MIT, p. 78-79, 1952

191
<table>
<thead>
<tr>
<th>No.</th>
<th>Author(s)</th>
<th>Title and Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>52-08</td>
<td>J.H. JANSEN and R. SUPPLEE</td>
<td>Impermeabilization of Cohesionless Soils by In-Situ Polymerization. M.S. Thesis, MIT, June 1952</td>
</tr>
<tr>
<td>52-12</td>
<td>M. NUMATA, T. MARUGASU and T. KUROSAKI</td>
<td>A New Method of Chemical Grouting to Solidify Loose Ground. Transactions, Japan Soc. of C.E., No. 12, 1952</td>
</tr>
</tbody>
</table>
52-14  W.E. BLACKBURN  
Process for Preparing a Grouting Fluid  
U.S.P. 2,618,570 - Nov. 18, 1952

52-15  G.G. WRIGHTSMAN  
Method for Consolidating or for Plugging Sands  
U.S.P. 2,595,184 - April 29, 1952

52-16  C. CARON (Ste. Soletanche)  
Procédé de rupture des emulsions bitumineuses ou  
analogues et applications, notamment en injection  
pour étancher ou consolider des sols perméables  
ou autres masses poreuses (Breakdown Procedure for  
Bituminous and Similar Emulsions and its Applica­  
tions, Especially in Grouting to Waterproof or  
Consolidate Permeable Soils and Other Porous Masses)  
F.P. 1,051,782 - Feb. 23, 1952

52-17  R.W. BURROWS, H.J. GIBBS and H.M. HUNTER, Compilers  
Progress Report on the Potential Uses of Lignin  
and the Chrome-Lignin Reaction in Bureau of Recla­  
mation Construction, General Report No. 15, U.S.  
Bur. of Recl., Design and Construction Div.,  
Denver, CO, Nov. 20, 1952

53-01  H. JAHDE  
Injektionen zur Verbesserung von Baugrund und Bau­  
werk (Injection for the Improvement of Foundation  
and Construction), Berlin Veb, Verlag Technik,  
Gerlin, 1953

53-02  Soil Stabilizing Permits Sand Augering  
Electrical West, Vol. 110, No. 5, p. 82-83, 1953

53-03  T.W. LAMBE  
The Effect of Polymers on Soil Properties  
Proceedings, The International Society on Soil  
Mechanics and Foundation Engrg., Zurich, 1953

53-04  Seepage Through Dam Checked by Injecting Chrome­  
Lignin, Engineering News-Record, Vol. 151, No. 15,  
p. 247, Oct. 8, 1953

53-05  S. SETO and K. OZAKI  
p. 815-817, 1953
53-06  K. SRECHY
Verschiedene Bodenverfestigungsweisen fur Fundamente (Various Types of Soil Consolidation for Foundation Work), Mernoki Touabbrepzo Intezet Kiaduanyag, Budapest, Hungary, 1953

53-07  BARKER and BECKER
Injection of Acrylate Monomers for Water-Sensitive Polymers, Book, 1953

53-08  S.H. PINNER

53-09  R. INOUE and T. YAMAUCHI

53-10  V.L. FOLT
Homopolymerization of Vinyl Chloride in Aqueous Medium
U.S.P. 2,625,539 - Jan 13, 1953

53-11  V.F.B. DE MELLO, E.A. HAUSER and T.W. LAMBE
Stabilization of Soils
U.S.P. 2,651,619 - Sept. 8, 1953

53-12  H. JOOSTEN
Das Joosten-Verfahren (The Joosten Method)
Harlem, Author's Edition, 1953

53-13  C. CARON and H. CAMBEFORT (Soletanche)
Procédé pour l’étanchement ou la consolidation des sols perméables ou autres masses poreuses et produit industriel permettant de mettre en œuvre le dit procédé (Procedure for Waterproofing or Consolidation of Permeable Soils or Other Porous Masses and the Industrial Product Which Makes it Possible)
F.P. 1,148,413 - July 16, 1953

54-01  J.P. GNAEDINGER

54-02  H.J. JOOSTEN
The Joosten Process, Published by Author, available from Chemical Soil Solidification Co., 7650 S. Laflin St., Chicago 20, IL, 1954

194
T.W. LAMBE and A.S. MICHAELS


J.P. GNAEDINGER

Chemical Solidification of Loose Sand as Aid in Tunnel Driving, Silicate P's and Q's, Vol. 30, No. 1, p. 2, first month, 1954

R. INOUE, T. YAMAUCHI and T. OZEKI

R. INOUE, T. YAMAUCHI and T. OZEKI
Chem. High Polymers (Japan), Vol. 11, p. 59-64, 1954

K. HAYASHI and S. OKAMURA
Chem. High Polymers (Japan), Vol. 11, p. 59-64, 1954

PAUL L. MENAUL

P.H. CARDWELL

E.G. HOWARD JR.
Polymerization of Ethylenically Unsaturated Compounds With Vanadous Catalyst U.S.P. 2,683,140 - July 6, 1954


H.J. JOOSTEN
Joosten Process for Chemical Soil Solidification and Sealing and Its Development from 1925 to date, 1954, N.V. Amsterdamche Ballast, Maatschappij
54-15  P.H. CARDWELL  
Treatment of Wells  
U.S.P. 2,674,322 - April 6, 1954

54-16  P.L. MENAUL  
Method of Sealing Porous Formations  

54-17  L.H. BROWN and P.G. HUETT  
Presented at 126th Meeting, ACS, New York, Sept., 1954

54-18  L.H. BROWN and P.A. WELLS  

54-19  E.R. NIELSEN  
U.S.P. 2,681,896 - June 22, 1954

55-01  JOHN P. GNAEDINGER  
Soil Stabilization by Injection Technique  

55-02  E.A. HAUSER  
Composition & Structure of Siliceous Compounds  
and Soil Stabilization, Silicic Science, p. 7-20, 141, 1955

55-03  R.K. ILER  
The Colloid Chemistry of Silica and Silicates  
Cornell University Press, Ithaca, NY

55-04  T.W. LAMBE  

55-05  R.C. MAINFORT  
Soil Stabilization With Resins and Chemicals  
Highway Research Board Bulletin No. 108, p. 112-120

55-06  G.E. MURRAY  

55-07  P.W. FISCHER and T.J. NOWAK  
Treatment of Oil-Bearing Formation  
U.S.P. 2,708,974 - May 24, 1955

196
55-08  R. LEFOULON and E. ISCHY
Usine de Fessenheim, 3e Bief du grand canal d'Alsace, protection des fouilles par injection des alluvions (Factory at Fessenheim, Third Reach of the Large Alsace Canal, Protection of Excavation by Injection of Alluvium), 5ème Congrès des grands barrages, Paris, 1955, R. 78

55-09  T.A. MARKUS
Soil Stabilization by Synthetic Resins

55-10  Grouting of Foundation Sands and Gravels
Corps of Engineers, Waterways Exp. Sta., Tech. Memo. 3-408, Vicksburg, MS, June 1955

55-11  M. ERCHAK and K.F. KOCH and H. KNUSTON

55-12  H.J. SOMMER, R.L. GRIFFIN
Asphalt Emulsions
U.S.P. 2,706,688 - April 19, 1955

55-13  T.J. NOWAK and P.W. FISCHER (Union Oil Co. of CA)
Selective Plugging in Oil Wells
U.S.P. 2,714,929 - August 9, 1955

55-14  C. CARON (Soletanche)
Produit pour l'étanchéification des sables fins
(A Product for Waterproofing Fine Sands)
F.P. 1,128,633 - July 1, 1955

55-15  W.C. HERAEUS (Applied on Nov. 3, 1952)
Improvements in or Relating to the Production of Polymerization Products
B.P. 734,948 - Aug. 10, 1955

56-01  Chemical Stabilization Cuts Excavation Cost

56-02  R. CEBERTOWICZ and R. MOLISZ
Jednoroztwarowe zeskalanie gruntu płaszczystego szklem wodnymi chemicznie wapnia, Politechnica Gdaska, Poland, 1956

56-03  C.M. RIEDEI

197
56-04  R. GEBERTOWICZA and K. ZIELINSKI
Zesralanie gruntu metoda
Panstwous Wydawnictwo Naukowe, Warsaw, Poland, 1956

56-05  Review of Materials & Methods for Dustproofing and

56-06  M. NUMATA, T. MARAGASU and T. KUROSAKI
A New Method of Chemical Grouting to Solidify Loose
Ground, Trans. Japan Soc. of Civil Eng., No. 12, 1956

56-07  H. NEUMANN
Injections de gels de silicate en vue de consolider
et étanchéifier le sol (Silicate Gel Injections
for Consolidating and Waterproofing Ground)
Die Bautechnik, Vol. 33, No. 6, June 1956

56-08  P.C. CARMAN
Flow of Gases Through Porous Media
Butterworth, London, 1956

56-09  P.G. CARPENTER
Sealing Porous Formations
U.S.P. 2,735,269 - Feb. 21, 1956

56-10  B. ROZGAL
Chemical Injections Based on Waterglass Solutions
Technicki Pregled, Vol. 8, p. 67-75 (in Russian),
C.A. Vol. 51, p. 3072a

56-11  SIMAKO et al
Resistance to Frost of Sands Stabilized by Chemical
Methods (in Russian), Sbornik Nauch Rabot beloruss,
politekh. Inst., No. 54, p. 57-62; C.A. Vol. 53,
11.795e

56-12  ERCHAK M. and R.J. BLAZEK
U.S.P. 2,775,579 - 1956

56-13  E.G. HOWARD
U.S.P. 2,729,624 - 1956

56-14  SEN and GHOSH
Studies on the Gelification of Silicic Acid Soil
Journal Indian Chem. Soc., Vol. 33, No. 6, 1956

56-15  K. KIETZ
Self Hardening Waterglass Compositions and Process
of Preparing Same
U.S.P. 2,766,130 - Oct. 9, 1956
<table>
<thead>
<tr>
<th>Reference Number</th>
<th>Author(s)</th>
<th>Title</th>
<th>Source(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>57-07</td>
<td>L.C. Vogel</td>
<td>Selective Plugging in Oil Wells</td>
<td>U.S.P. 2,796,934 - June 25, 1957</td>
</tr>
<tr>
<td>57-11</td>
<td>L.R. Schiffman and Ying Jer Shieh</td>
<td>Solid Business Builds on Shaky Foundations</td>
<td>Chemical Week, New York, NY, p. 56-57, July 6, 1957</td>
</tr>
</tbody>
</table>
57-13 H. CAMBEFORT and C. CARON

57-14 M. DONEL
The Durability of Joosten Solidified Material
Die Bautechnik, Berlin, W. Germany, Vol. 11, No. 6, p. 222-255, June 1957

57-15 LO RE V.
Areias de fundacao aglomeradas por silicato de sodio e gas carbonico (Foundation Sands Consolidated with Sodium Silicate and Carbonic Gas)
Boletim Assoc. Brasileira de metais, Vol. 13, p. 129-137, No. 47

57-16 J. KELL
Pre-Treatment of Gravel for Compressed Air Tunneling Under River Thames at Dartford
Chartered Civil Engineer, p. 20-24, March 1957

57-17 C. CARON (Soletanche)
Nouvelle méthode de gelification des silicates alcalins ou l'application des produits nouveaux en résultant à l'étanchement ou à la consolidation des sols ou autres masses poreuses (New Method Using Alkaline Silicate Gels or New Products to Waterproof or Consolidate Soil and Other Porous Masses)
F.P. 1,164,835 - Jan. 18, 1957

57-18 W.C. HERAEUS (Applied in 1955)
B.P. 771,631 - April 3, 1957

57-19 R.W. ROTH
Soil Stabilization
U.S.P. 2,801,985 - August 6, 1957

57-20 H.F. KELLER, JR. et al (Union Oil Co. of California)
Selective Plugging of Subterranean Formations
U.S.P. 2,792,893 - May 21, 1957

58-01 ROBERT L. SHIFFMAN and CHARLES R. WILSON
R.O. PYNNONEU and A.D. LOOK

C.M. RIEDEL

H.Q. GOLDER

R. BARBEDETTE and F. SABARLY
Contribution à l'amélioration technique et économique de la silicatisation (Contribution to the Improvement of the Technical and Financial Aspects of Silicate Grouting), 6th Internat'l Congress on Large Dams, New York, 1958

R.N. DOGRA and I.S. UPPAL
Chemical Stabilization of Sand and Sandy Soils Laboratory Experiments With Sodium Silicate as Stabilizer, Journal Indian Roads Congress, Vol. 23, No. 1, p. 161-172

R.W. NIELD and D. EPSTEIN

N.M. ZIMAKO and M.A. IOSELEVA
Effect of Various Sulfate on the Strength of Fixation of Sandy Soil During Silicatization (in Russian), C.A. 54 13.601h, 1960; Belorusse Polytech. in L.V. Stalina, No. 59, p. 149-153

Y.M. DENISOV and B.F. RELTOV

GANDON, LEHMANN, MARCHEGUET and TARBORIEGH
Gel transformable en une masse ayant les propriétés d'un ciment et procédé de préparation de ces produits (A Gel Which Converts to a Mass Having the
Properties of Cement and the Method of Preparation for Same)
F.P. 1,166,581 - 1958

58-11
J.J. PADBURY (American Cyanamid Co.)
Soil Stabilization With Polymerized Monomeric Triazine and Product
U.S.P. 2,838,466 - June 10, 1958

58-12
P.G. CARPENTER
Sealing Porous Formation
U.S.P. 2,858,892 - Nov. 4, 1958

58-13
R.C. JOHNSTON and N.W. KOZIAKIN
Foundation Design and Methods Cut Skyscraper Cost

58-14
H. GARTON EMBLEM and J. ASTON
Mould and Method of Making the Same
U.S.P. 2,829,060 - April 1, 1958

58-15
A. WESTON and R.A. KENNERLEY
The Dichromate Lignosulphonate Reaction and Its Potential Use in Chemical Grouting
New Zealand Journal of Science, Vol. 1, No. 1, p. 9-17, March 1958

59-01
J.W. MC BEAN and L.J. CUNNINGHAM
Canadian Experiences With AM-9 Chemical Grout
9th Annual Drilling Symposium, Pennsylvania State Univ., Oct. 9, 1959

59-02
SCHMIDT and GEDEK
Produit d'étanchement et de consolidation pour des terrains et maçonnés (Product for Waterproofing and Consolidation of Soils and Masonry)
G.R.P. A 39 - 14/59 - May 26, 1959

59-03
J.S. MAGLELNICKI
Base Waterproofing Harvard University's Cambridge Electron Accelerator
American Cyanamid Co., August 10, 1959

59-04
R.H. KAROL

202
59-05 F.G. ATHERTON and W.S. GARRETT  
The History of Cementation in Shaft Sinking  
Proceedings, Conf. on Shaft Sinking and Tunneling, 
London, p. 394, July 1959

59-06 Grout Under Base Cuts Compressor Vibrations  
Engineering News-Record, New York, NY, Vol. 163,  
p. 55, July 2, 1959

59-07 L. BILHEIMER  
Chemical Grout Technique Solves Meramec Shaft  
Sinking Problem, Engineering and Mining Journal,  

59-08 R.W. GAUL and A.J. APTON  
Epoxy Adhesives in Concrete Construction  
Civil Engineering, ASCE, Nov. 1959

59-10 R.E. MOREY and E.A. LANGE  
Factors Affecting Sodium Silicate Bonded Sands  
Foundry, p. 188-198, April 1959

59-11 Stabilization of Soils With Sodium Silicates  
Massachusetts Institute of Technology, MIT,  
Soil Stabilization Report, Phase 11, p. 48-62, 1959

59-12 P. NELSON  
Rocky Reach Grouting, Pacific Builder and Engineer,  
Seattle, WA, Vol. 65, p. 76-78, March 1959

59-13 BOZEL-MALETRA  
Gel transformable en une masse ayant les propriétés  
d'un ciment et procédé de préparation de ces  
produits (A Gel Which Converts to a Mass Having  
the Properties of Cement and the Method of Preparation  
of Same)  
R.P. 1,166,581 - 1959

59-14 R.W. ROTH (to American Cyanamid)  
Method for the Stabilization of Soils (Australia)  
Australian Patent 222,316 - June 23, 1959

59-15 P. PEELER  
Chemical Composition and Process  

59-16 G.G. NATUSCH  
Hawea Lake Control Works, New Zealand Engineering,  
Dec. 15, 1959

203
C. CARON (Ste. Soletanche)
Procédé d'injection des terrains peu perméable, par formation d'une résine phénoplaste (Procedure for Grouting Slightly Permeable Soil Through the Use of a Phenoplast Resin)
F.P. 1,248,651 - Nov. 13, 1959

C. CARON (Ste. Soletanche)
Nouveau procédé d'injection de coulis d'argile et produit utilisé pour la mise en oeuvre du dit procédé (New Injection Procedure With Clay Grout and the Product Used for Said Procedure)
F.P. 1,237,311 - June 19, 1959

H. BURK
Die Verbesserung des Betons im Tiefbau des Donaukraftwerkes Kochlet durch Injektionen (Grouting to Strengthen the Concrete in the Foundation of Kochlet Power Station on the River Danube)

R.H. KAROL
Field Experimentation, Gaisson-Bell Grouting
American Cyanamid Co., June 1960

J.W. MC BEAN and L.J. CUNNINGHAM
Chemical Grouting as Aid in Diamond Drilling
Canadian Mining Journal, Gardenvale, Quebec, Canada, p. 74-75, April 1960

Chemical Grout to Seal and Bind Loose Soil

R.H. KAROL

Soil Stabilization with Sodium Silicates
MIT, Soil Stabilization Report, Phase XII, p. 29-46, 1960

R.L. HANDY, J.L. JORDAN, L.E. MANFRE, D.T. DAVIDSON
G.B. VAISFEL'D

V.L VOLKOVA

N.M. ZIMAKO and M.A. IOSELEVA
The Consolidation of Sand by the Introduction of Mixed Salts in the Reaction with Sodium Silicates C.A. 5611, 242a, 1962

REED JOHN J. and BILHEIMER LEE

H. RAKOWITZ
Control System for Soil Stabilizer Polymerization U.S.P. 2,940,729 - June 14, 1960

D.R. FREITAG and G.R. KOZAN

P.T. SHERWOOD

FERN K.A. and W.H. MONTGOMERY
Quelques applications du coulis chimique AM-9 (Some Applications for AM-9 Chemical Grout) Schweiz Gesellschaft für Bodenmechanik und Foundationstechnik (Swiss Assoc. for Soil Mechanics and Foundation Technology), Mitteilung No. 46, 1961

R.C. CHELLIS
<table>
<thead>
<tr>
<th>61-06</th>
<th>A. BLATTER</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vorversuche und Ausführung des Injektionsschleiers in Mattmark (Test Section and Actual Grouting in Mattmark), Schweizerische Bauzeitung, Vol. 79, No. 42-43, p. 723-728, 739-746, 1961</td>
<td></td>
</tr>
</tbody>
</table>


<table>
<thead>
<tr>
<th>61-08</th>
<th>H. CAMBEFORT</th>
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</thead>
<tbody>
<tr>
<td>L'injection et ses problèmes (Injection and its Problems), Bulletin technique de la Suisse Romande, No. 19, Sept. 23, 1961</td>
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</table>

<table>
<thead>
<tr>
<th>61-09</th>
<th>L.A. YORK</th>
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<tbody>
<tr>
<td>Shaft Sinking With Chemical Grout, Coal Age, New York, Vol. 66, No. 9, p. 72-75, Sept. 1961</td>
<td></td>
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</tbody>
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<thead>
<tr>
<th>61-10</th>
<th>JOHN C. KING and EDWARD G. W. BUSH</th>
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<th>61-14</th>
<th>H.Q. GOLDER, H.J.F. HARDING and R.A. SEPTON JENKINS</th>
</tr>
</thead>
</table>
61-15 J.F. RAFLE & D.A. GREENWOOD
Relation Between Rheological Characteristics of
Grouts and Their Capacity to Permeate Soil
Proceedings, 5th Internat'l Conf. of Soil Mechanics

61-16 J.T. LEONARD
Grouting: Clay-Based and Chemical, The Engineer,

61-17 Final Report on the Engineering Properties of
Three Sand Gel Systems, Massachusetts Inst. of
Tech. (MIT), Report No. 121, Aug. 1961

61-18 P.A.R. COME
Procédé de préparation d'un liant universel et
d'agglomérés correspondants (Procedure for Preparing a Universal Binder and Corresponding Con­glomerates)
F.P. 1,294,158 - April 16, 1961

61-19 C. CARON (Ste. Soletanche)
Method and Composition for Strengthening Loose
Grounds
U.S.P. 3,012,405 - Dec. 12, 1961

61-20 Chemical Consolidation in Civil Engineering Prac­tice, Geotechnical Pamphlet No. 7, Soil Mechanics,
Ltd., 1961

61-21 R. GLOSSOP
The Invention and Development of Injection Process,

61-22 C. PEELER
Chemical Composition and Process for Soil Stabiliza­tion

61-23 Societe NOBEL-BOZEL
Gels de silice transformables en une masse très
cohérente et très dure et leur procédé de préparation
(Silica Gels Which Can Convert to a Highly
Cohesive and Very Hard Mass and Their Method of
Preparation)
F.P. 1,298,359 - May 12, 1961
Agent for the Chemical Sealing and Solidification of Earth Layers and Buildings
B.P. 865,744 - March 19, 1961

E. STOSSEL
Preparation of Colloidal Dispersions of Fine Particle Size Silica Hydrogel in Polyols

Ste. Soil Mechanics Limited
Perfectionnement au traitement des sols granulaires (Improvement of Granular Soils Through Treatment)
F.P. 1,285,092 - March 29, 1961

Ste. Soil Mechanics Limited
Procédé de renforcement de sols granuleux (Procedure for Strengthening Granular Soils)
F.P. 1,289,294 - May 17, 1961

W.F. HOWER

R.A. JONES and V. KONDIC

R.K. KATTI and K.R. KULKARNI

L.A. YORK


L.V. STEVENS
Chemical Grouting, Mining Congress Journal, p. 56, Jan. 1962

208
62-07  J.J. REED  

62-08  Tough Tunnel Bows to Chemical Grouting  


62-10  Chemical Grout Seals Shafts Through Wet Sand  
Construction Methods and Equipment, Vol. 44, p. 140, 144, 147, May 1962

62-11  L.J. CUNNINGHAM  

62-12  A. PIAKOWSKI  
Some Cases of Applying Injection Method to Counteract Harmful Settlement of Buildings  

62-13  Soil Consolidation in the Soviet Union  
J. Crossfield & Sons, Ltd., Warrington, 24 pp, 1962

62-14  R.H. KAROL and L.E. MARK  
Unique Use of Chemical Grout Solution Promises Precise Sampling of Loose Soil, Engineering and Mining Journal, New York, June 1962

62-15  T.W. LAMBE  

62-16  L.A. YORK  
Grouting by Cementation  
Mining Congress Journal, p. 51, Jan. 1962

62-17  E. ISCHY and R. GLOSSOP  

209
62-18 R. CHADEISSON
Quelques résultats de traitements par injection de terrains sans cohésion (Efficacité et permanence) (Some Results of Loose Terrain Treated by Grouting (Effectiveness and Permanence)
Le Genie Civil, Sept. 1 and Sept. 15, 1962

62-19 T.W. LAMBE

62-21 C. CARON, C. GAILLEDREAU and Y. BELOT

62-22 K. SAIN

62-23 W.F. SWIGER

62-24 R.H. MC DOWELL and B.T. TATHAM
Alginate: Formation of a Gel by Reaction Between Sodium Alginate and a Metal Salt B.P. 908,868 (to Alginate Ind., Ltd.) Oct. 24, 1962

62-25 D.H. RAKOWITZ (to American Cyanamid Co.)

62-26 S.J. REHMAR, N.L. LIVER (to Intrusion Prepakt, Inc)

62-27 GANDON et al
U.S.P. 3,028,340 - April 1962
M. HAFFEN

K. BILLIG

H.H. SPAIN

C.H. WAKEMEN, H.E. STOVER and E.N. BLYE

H.H. SPAIN

F. JAFFE and H. KAESMACHER

A.L. LITTLE, J.C. STEWART and P.J. FOOKES

A.W. SKEMPTON and P. CATTIN
<table>
<thead>
<tr>
<th>Reference</th>
<th>Authors</th>
<th>Title</th>
</tr>
</thead>
<tbody>
<tr>
<td>63-04</td>
<td>C. CARON, J.P. DELISLE and W.H. GODDEN</td>
<td>Resin Grouting, With Special Reference to the Treatment of the Silty Fine Sand of the Woolwich and Reading Beds at the New Blackwall Tunnel, ibid., p. 142, May 1963</td>
</tr>
<tr>
<td>63-05</td>
<td>K.A. FERN</td>
<td>The Application of Polymerization Techniques to the Solution of Grouting Problems, ibid., p. 146, May 1963</td>
</tr>
<tr>
<td>63-06</td>
<td>R.J. NEELANDS and A.N. JAMES</td>
<td>Formulation and Selection of Chemical Grouts with Typical Examples of Their Field Use, ibid., p. 150, May 1963</td>
</tr>
<tr>
<td>63-07</td>
<td>M.W. LEONARD and K. MOLLER</td>
<td>Grouting for Support with Particular Reference to the Use of Some Chemical Grouts, ibid., p. 156, May 1963</td>
</tr>
<tr>
<td>63-08</td>
<td>B.O. SKIPP and L. RENNER</td>
<td>The Improvement of the Mechanical Properties of Sand, ibid., p. 29, May 1963</td>
</tr>
<tr>
<td>63-10</td>
<td>G.K. JONES</td>
<td>Chemistry and Flow Properties of Bentonite Grouts ibid., p. 22, May 1963</td>
</tr>
<tr>
<td>63-12</td>
<td>D.A. GREENWOOD and J.F. RAFFLE</td>
<td>Formulation and Application of Grouts Containing Clay, ibid., p. 127, May 1963</td>
</tr>
</tbody>
</table>
63-14 W.E. PERROTT and P.F.F. LANCASTER-JONES
Case Records of Cement Grouting, ibid., p. 80, May 1963

63-15 M.G. MANVELYAN et al
Reaction of Aqueous Solutions of Lithium and Potassium Carbonate with Calcium Metasilicate

63-16 Dustproofing and Waterproofing of Soils
Laboratory Studies of Soil Waterproofing Materials.

63-17 SOLETANCHE
Contribution of Grouting to the Dam Technique
"New Horizons" - Topmost Dams of the World, Japan Dam Assoc., Tokyo, 1963

63-18 JOHN DRAKE
Chemical Grout Seals Sheet Piles
Western Construction, San Francisco, CA, Jan. 1963

63-19 W. J. HOLMES
Electro-Osmosis and the Civil Engineer, Civil Engineering and Public Works Review, London,
Vol. 58, No. 682, p. 624-626, May 1963

63-20 ROBERT M. GERZETICH
Plastic Injection Solves Tunnel-Seepage Problem
Electric Light and Power, Chicago, IL, Oct. 1963

63-21 Report of Laboratory Pilot Studies for Rock Bonding
with Chemical Grout, Technical Report No. 2-31,
Cincinnati, OH, June 1963

63-22 G. GRESCHIK
Anwendung der chemischen Bodenverfestigung zum
Schliessen einer Baugrube mit einer einzigen
Losung (Chemical Soil Consolidation to Close a
Construction Excavation with a Single Solution)
Proceedings, Intern. Conf. on Soil Mechanics and
Foundation Engrg., Budapest, p. 385-395, Sept. 24-
27, 1963

213
V. CZIGLINA

G. PETRASOVITS
Tests on Chemical Grouting and Waterproofing by Using Aminoplast Resins (in German), ibid., p. 429-440, Sept. 24-27, 1963

J. JOHNSON STUART
Chemical Grouting Licks Heavy Sewer Infiltration Wastes Engineering, 34, No. 3, p. 130-132, 1963; C.A. 58 1359Sh, 1963

G. WILTON
TV and Chemical Grout, American City, New York, Vol. 78, p. 78-9, Aug. 1963

Under Dams or Over Subways, Chemical Grout Plugs Leaks, Engineering News-Record, NY, Vol. 171, Aug. 8, 1963

C.A. PEGUIGNOT

T.J. O'BRIEN

Z.L. JANUS
Chemical Grout Cuts Waterflow in Colliery Drift Mines and Quarry Mechanization, 1963

Report of Investigation of Chemical Grouts for Rock Bonding, U.S. Army Engineer Dist., Omaha, 1963

L.A. LUNDBERG, J.C. SCHLEGEL, J.E. CARPENTER
Resinous Composition (to American Cyanamid Co.) U.S.P. 3,091,936 - June 4, 1963

C.E. WATSON (to California Research Corp.)
63-36  A.R. HILTON, JR. and H.H. SPAIN
Sand Consolidation
U.S.P. 3,100,527 - Aug. 13, 1963

63-37  SOLETANCHE
Improvements in or Relating to the Stabilization of Soil
B.P. 918,641 - Feb. 13, 1963

63-38  Grouts and Drilling Muds in Engineering Practice,
Symposium organized by the British National Society of the International Society of Soil Mechanics and Foundation Engineering at the Institute of Civil Engineers, Discussion, p. 164, May 1963

63-39  STEFAN

64-01  R.H. KAROL

64-02  Sealing Leaks from the Inside Speeds Work and Cuts Cost of Sewer Rehabilitation Program
The American City, New York, June 1964

64-03  Chemical Grout Licks Tough Quicksand Problem
Railway Track and Structures, Chicago, IL, p. 20-22, Feb. 1964

64-04  D.C. MC LEAN
Use of Resins in Mine Roof Support, Mining Engineering, New York, Vol. 16, No. 1, p. 36-40, Jan. 1964

64-05  W.E. PERROTT
Chemical Grouting on New Blackwall Tunnel
Civil Engineering and Public Works Review, London, April 1964

64-06  Chemical Grout Stabilizes Soil to Permit Jacking

215
64-07 NH Solves a Quicksand Problem, Railway Age, New York, p. 19-22, Feb. 3, 1964

64-08 G.P. TSCHEBOTARIOFF
Vibration Controlled by Chemical Grouting
Civil Engineering, ASCE, p. 34-35, May 1964

64-09 J.H. THATCHER
A Difficult Foundation Problem Solved with the Aid of Chemical Soil Solidification,

64-10 R. NOOE
Seal Sewer Leaks from the Inside, The American City, New York, June 1964

64-11 C.M. RIEDEL

64-12 H. CAMBEFORT
Injection des sols (Ground Grouting)

64-13 C. CARON
Injection des résines organiques dans les fines fissures du béton (Grouting Fine Fissures in Concrete with Organic Resins), Construction, April, 1964

64-14 Report of Investigation of Chemical Grouts for Rock Bonding, U.S. Army Engineer Dist., Omaha, Corps of Engrs., Omaha, NB, July 1963 and March 1964

64-15 D.G. CAMPBELL and J.R. DALY

64-16 Dough Mixer Batches Up Epoxy Armor

64-17 H.L. HOOVER
Water Leakage Inhibiting Masonry Treatment
U.S.P. 3,127,705 - April 7, 1964
Technical and Informational Bulletins
Philadelphia Quartz Company, 1964

LOUIS GANDON
Preparation of Silica Gels from Alkaline Silicates
and Polyalcohol
U.S.P. 3,149,985 - Stp. 22, 1964

T.J. ROBICHAUX
Method of Treating Earth Formations

R.E. WRIGHT
Chemical Grouting with Silicate-Bicarbonate and
Silicate-Aluminate Mixtures
Philadelphia Quartz Co. of CA, Conf. Presented at
Chemical Grout Symposium, Engineers Club of San
Francisco, Jan. 24, 1964

E.R. NIELSEN
U.S.P. 3,158,592 - Nov. 24, 1964

J. JANIN
Les produits chimiques de traitement et de consoli-
dation des sols (Chemicals Used in the Treatment
and Consolidation of Grout), Revue Arts et Manu-
factures, No. 149, Jan. 1965

H. CAMBEFORT et al
Dilution des coulis newtoniens injectés dans les
sols pulvérulents (Dilution of Newtonian Grouts
Injected into Powdery Soils), Le Genie Civil,
p. 1 and 15, June 1965

C. CARON
Consolidation des sables par injection de gel de
silice (Consolidation of Sands by Injections of
Silica Gel), Annales de l'ITBTP - Essais et
mesures, Sept. 1965

C. CARON
Etude physico-chimique des gels de silice
(Physico-Chemical Study of Silica Gels)
Annales ITBTP - Essais et mesures (81), p. 447-484,
March, April 1965

217
65-05  W.E. PERROTT
British Practice for Grouting Granular Soils
Journal of the Soil Mechanics and Foundations
Div., ASCE, Vol. 91, No. SM6, Proc. Paper 4542,
p. 57-79, Nov. 1965; Reprint No. 167, ASCE Water
Resources Engrg. Conf. at Mobile, AL, March 8-12,
1965

65-06  Epoxy Seals Leaking Salt Mine Shaft, Engineering
News-Record, New York, Nov. 18, 1965

65-07  G.R. KOZAN and W.B. FENWICK
Soil Stabilization, Corps of Engineers, Tech.
Report No. 3-465, Rpt. 7, U.S. Army Engineer
Waterways Experiment Sta., Vicksburg, MS, 1965

65-08  F. DIERNAT and J. DE LA JARRIGE
Use of Resins for Repairing Concrete Grouting
Cracks and Waterproofing the Face of a Dam
Translation No. 65-4, U.S. Army Engineer Waterways
Experiment Station, Vicksburg, MS, 1965

65-09  Continental Oil Company
Procédés de consolidation de couches souterraines
(Procedures for Consolidating Subterranean Layers)
P.F. 1,444,013 - 1965

65-11  JOE T. MOORE, JR.
Controlling Leakage from Cowans Ford Dam
Civil Engineering, ASCE, Vol. 35, No. 6, p. 52,
June 1965

65-12  DARIUS BONAZZI
Alluvium Grouting Proved Effective on Alpine Dam
Journal of the Soil Mechanics and Found. Div.,
ASCE, Vol. 91, No. SM6, Proc. Paper 4544, p. 81-
93, Nov. 1965

65-13  Aswan High Dam
The Engineer, London, Vol. 219, p. 716, April 23,
1965

65-14  WALDO G. BOWMAN
Aswan Dam; Crucial Phase: Grouting the Riverbed
Engineering News-Record, NY, Vol. 175, No. 24,
p. 48-56, Dec. 9, 1965

65-15  H.C. M. LAUGHLIN (to Halliburton Co.)
Preparation and Use of Sodium Silicate Gels
65-16  J.J. FLOVEY  (to American Cyanamid Co.)
Process for Stabilizing Soil
U.S.P. 3,208,226 - Sept. 28, 1965

65-17  R.J. GOODWIN and F.L. BECKER  (to Gulf R & D Co.)
Grouting Method
U.S.P. 3,221,505 - Dec. 7, 1965

65-18  R.R. KOCH, J. RAMOS, H.C. MC LAUGHLIN
(to Halliburton Co.)
Composition and Method for Stabilization of Soil

65-19  Composition pour la consolidation des sols-Progil
(Composition for Ground Consolidation-Progil)
F.P. 1,458,945 - Jan. 25, 1965

65-20  Réactifs gelifiant pour silicates solubles
Progil (Setting Reagents for Soluble Silicates, Progil)
F.P. 1,476,636 - Dec. 28, 1965

65-21  B.M. YOUNG
Method of Consolidating Incompetent Sands and
Composition Therefor.
U.S.P. 3,199,590 - Aug. 10, 1965

65-22  I. METIL

65-23  J. GRANIER
Contribution à l'étude des résines polymerisables
à froid en milieu aqueux (Contribution to Re­
search on Unheated Polymerizable Resins in an
Aqueous Medium), Mémoire présenté à l'Ecole
Nationale Supérieure des Laboratoires, Paris, 1965

66-01  Bibliography on Chemical Grouting, Third Progress
and Found. Div. Proceedings, ASCE, SM6, Paper
No. 4969, p. 39-66, Nov. 1966

66-02  Chemical Grout Curtain Stops Water-Flow Through
Fine Sands, Construction Methods and Equipment,
p. 94-97, July 1966

219
66-03  C. CARON
Etude physico-chimique des gels de silice - Application aux problèmes d'injection (Physico-Chemical Study of Silica Gels, Grouting Applications), Colloque "Oxydes", Brussels, 1966

66-04  D.R. WILLIAMS (to Cementation Co., Ltd., London)
Silicate Grout
U.S.P. 3,294,563 - Dec. 27, 1966

66-05  RAYONIER, INC. (U.S.A.)
Procédé de consolidation du sol (Ground Consolidation Procedure)
F.P. 1,469,842 - Feb. 22, 1966

66-06  The Borden Chemical Co. Ltd. (U.K.)
Procédé pour la stabilisation du sol (Ground Stabilization Procedure)
F.P. 1,514,159 - Nov. 10, 1966

66-07  F.G.P. LAZARE
Réalisation d'une étanchéité à travers une paroi par injection de résines polymérisables à forte expansion lors de la polymerisation (Waterproofing Through a Wall by Injection of Polymerizable Resins Which Expand Greatly Upon Polymerization)
F.P. 1,488,804 - Aug. 5, 1966

66-08  F.E. DOLLARHIDE et al (Dow Chemical)
Procédé pour empêcher la circulation de l'eau dans les passages existant dans le sol et agrégat granulaire utilisé dans ce procédé (Process for Stopping Water Seepage in the Ground and the Granular Aggregate Used in this Process)
F.P. 1,487,607 - July 22, 1966

67-01  C. CARON
Applications des résines synthétiques dans les travaux publics (Applications of Synthetic Resins in Public Works), Annales ITBTP, Série matériaux, July-Aug. 1967

67-02  J. JANIN
Les produits chimiques de traitement et de consolidation des sols (Chemicals Used in Ground Treatment and Consolidation), (See also Reference 65-01), Revue technique du bâtiment et des constructions industrielles (Technical Review of Building and Industrial Structures), No. 3, p. 81-85, Nov.-Dec. 1967
67-03  I.C. HILTON
Grout Selection: A New Classification System

67-05  G.A. MILLER (to Diamond Alkali)
Composition and Method for Stabilizing Soil

67-06  R.M. JORDA, T.J. ROBICHAUX, S.G. GIBBS
Method of Stabilizing Piles (to Shell Oil Co.)
U.S.P. 3,324,665 - June 13, 1967

67-07  C. CARON (to Soletanche, Paris)
Method for Injecting the Components of a Phenoplastic Resin into Slightly Watertight Grounds

67-08  H.C. MC LAUGHLIN (to Halliburton Co.)
Method of Stabilizing or Sealing Earth Formations
U.S.P. 3,334,689 - Aug. 8, 1967

67-09  C.E. PEELER, A.D. BERGMAN, D.J. OLIX
(to Diamond Alkali)
Composition of Stabilizing or Sealing Earth Formations
U.S.P. 3,335,018 - Aug. 8, 1967

67-10  G. CSANDA, G. CZERZY, I. DEZSENYL, L. NOVAK
Procédé pour rendre étanches des éléments de construction, canaux, conduits ainsi que des fentes, porosités et espaces creux dans le sol et consolider celui-ci (Method of Waterproofing and Consolidating Elements of Construction, Canals, Conduits as Well as Crevices, Porosities, and Hollow Spaces in the Soil)
F.P. 1,553,689 - March 6, 1967

67-11  MARK and GAYLORD
Encyclopedia of Polymers and Science Technology,

68-08  H. OGER
Memoire présenté à l'école supérieure de labo.
Contribution à l'étude des résines de collage pour les forages et les injections (Contribution to Research on Gluing Resins for Drilling and Injections), 1968

221
| 68-09 | G.A. SERLACHIUS OY, LIELAHTI |
|       | Gels and Process for Preparing the Same |
|       | B.P. 1,241,502 - Sept. 27, 1968 |

| 68-10 | M. GOUREVITCH and R. BARBEDETTE |
|       | Nouveau mélangé polymerisable à froid pour l'injection des sols et ouvrages de toute nature |
|       | (New Unheated Polymerizable Mixture for Grouting Ground and Construction Work of All Types) |
|       | F.P. 1,566,481 - March 6, 1968 |

| 68-11 | H.B. ERICKSON |
|       | Strengthening Rock by Injection of Chemical Grout |

| 68-12 | R.H. KAROL |

| 68-13 | C. KUIZNER |
|       | About the Mechanical Properties of Soils Injected with Silicate Gels, Die Bautechnik, No. 3, 1968 |

| 68-14 | J. RAMOS and R.F. RENSVOLD (to Halliburton Co.) |
|       | Soil Stabilization and Grouting Method |
|       | U.S.P. 3,374,934 - March 26, 1968 |

| 68-15 | F.W. HERRICK, R.I. BRANDSTROM (to Rayonier, Inc.) |
|       | Process for Grouting with a Tri-Component Chemical Grouting Composition |
|       | U.S.P. 3,391,542 - July 9, 1968 |

| 68-16 | ROGER F. RENSVOLD (to Halliburton Co.) |
|       | Epoxy Resin Grouting Fluid and Method for Stabilizing Earth Formations |

| 68-17 | E. HIGASHIMURA, M. ISHII, Y. ISHIKAWA |
|       | Soil Stabilization (to Mitsubishi Rayon, Tokyo) |

| 68-18 | L.E. VAN BLARICOM, H.R. DEWEYERT, N.H. SMITH |
|       | Grouting Composition (to ITT Rayonier Corp.) |
69-01  O.G. INGLES
Soil Stabilization in the Building Industry
Div. of Soil Mechanics, Tech. Memo. No. 9,
Commonwealth Scientific & Industrial Research
Organization, Australia, 1969

69-02  I.P. CERNYJ and M.N. IBRAGIMOV
Experiences in the Stabilization of Water-Saturated
Sands with Carbamic Resins, Osnov fund. Mech.
Grunt 11, No. 1, p. 30-32, 1969

69-03  C. CARON
Injections spéciales/ réparation, consolidation,
étanchéité (Special Injections: Repair, Consol­
dation, Impermeability), Annales de l'institut
technique de bâtiment et des travaux publics,

69-05  Le prolongement de la ligne 13 du reseau souterrain
de la RATP entre Saint Lazare et Miromesnil
(The Extension of the No. 13 Line of the Under­
ground Transit Part of the Paris Rapid Transit
System Between Saint Lazare and Miromesnil)
Chantier de France, Sept.-Oct., 1969

69-07  G. CZERNY and Z. REGELE
A New Method of Soil Stabilization Supersilic
Acta technica Academiae Scientiarum Hungaricae,
61 (1-2), p. 77-87, 1969

69-08  L.H. EILERS, C.F. PARKS (to Dow Chemical Co.)
Grouting, Plugging and Consolidation Method

69-09  L.I. KORZHENKO and E.I. MULYUKOV
Experience in Grouting Bashkir Soils with Urea
Formaldehyde Resin, Osnovaniya, Fundamenty i
Mekhanika Gruntov, No. 4, p. 23-25, July-Aug., 1969

69-10  Un nouveau procédé chimique aqua-réactif de stabi­
lisation des sols (TACSS System) (A New Water­
Reactive Chemical Process for Ground Stabilization)

69-11  C.F. GARCIA
Liquid Preflush Composition and Use Thereof in
Acidizing Earth Formations
DR. ING. KARL RUDOLF DEMWOLFF
Verpressen mit heissem Bitumen (Grouting with Heated Bitumen), Revue Bitumen-Teere-Asphalte-Pech und verwandte Stoffe, May 1969

J.K. MITCHELL

EINSTEIN H.H. SCHMITTER
Selection of Chemical Grout for the Mattmark Dam, ibid., 96, No. SM 6, p. 2007, 1970

P.A. BOURGE
Etude de la stabilisation des sols aux résines (Survey on Ground Stabilization with Resins) Université de Liège, Thèse pour l'obtention du grade d'ingénieur civil des constructions (Thesis for degree in construction civil engng.) 1969-70

J. DESCHAMPS

J. JANIN and G. LE SCIELLOUR

A.C. PLAISTED and R.G.H. BOYES
Selection and Use of Chemical Grouts Contract Journal, July 23, 1970

C. CARON
Rhéologie des coulis d'injection (Grout Rheolgy) Communication au Comité Technique de la Société Hydrotechnique de France (Communique to the Technical Committee of the Hydrotechnical Assoc. of France), March 20, 1970

H.L. JESSBERGER
C. CARON

J. CIESIELSKI
Renforcement par injection de résine époxyde des constructions en béton armé endommagées (Reinforcement of Damaged Reinforced Concrete Structures by the Injection of Epoxy Resin), ibid., Vol. 2, p. 304, 1970

W. FRANKE

H. HAMALGIU, I. VASILESCU, D. HALISKI
Utilisation de polymères dans une usine de pré-fabriqués pour la réparation des éléments en béton armé et précontraint (Use of Polymers in a Prefabricated Elements Factory for the Repair of Prestressed and Reinforced Concrete Elements) ibid., Vol. 2, p. 375, 1970

H. KRAK
Cracking of Concrete and the Influence on Epoxy Resin Based Coatings, ibid., Vol. 2, p. 401, 1970

J. MURATA, K. KOBAYASCHI
Durability and Watertightness of Concrete Impregnated with Epoxy Resins, ibid., Vol. 2, p. 439, 1970

P. SMITH, B. CHOJNACKI, K. LANGHAMMER
Performance Evaluation of Concrete Restoration Materials and Methods, ibid., Vol. 2, p. 509, 1970

Y. TSURUTA
Study on Repairing of Cracks, ibid., Vol. 2, p. 539, 1970

H.P. WERSE
The Repair of Fissures in Concrete Structures, ibid., Vol. 2, p. 581, 1970
70-18  I.M. ELSHIN
Experience in Using Plastic Concrete with Furan Resins in Different Structures, ibid., Vol. 1, p. 344, 1970

70-19  I. IONESCU, I. FALAORU
Quelques résultats de recherches de laboratoire et semi-industrielles concernant les bétons à base de résine furfural-acetonique "F.A." (Some Results from Laboratory and Semi-Industrial Research on Furfural-Acetonide-Base Concretes), ibid., Vol. 1, p. 397, 1970

70-20  V.A. KARGUINE
Prévisions relatives à l'utilisation des polymères pour la consolidation des sols (Estimates for the Use of Polymers in Ground Consolidation)

71-01  HURLEY and THORN BURN

71-02  Réactifs gelifiant pour silicates solubles (Setting Reagents for Soluble Silicates)
Progil
F.P. 2,151,648 - Sept. 1, 1971

71-03  Procede de stabilisation de la terre (Ground Stabilization Process)
Toho Chemical Industry Co., Ltd.
F.P. 2,109,614 - June 10, 1971

71-04  M. PEIGNAUD
Consolidation par injections des fondations du pont de Saumur, France (Consolidation through Grouting the Foundations of the Saumur Bridge)
V. LELU and R. PFLIEGER

J.P. VAN LOON
Mémoire présenté au Conservatoire des Arts et Métiers à Paris (Report presented to the Conservatory of Arts and Trades in Paris), 1971

V.F. DEMINE
Coulis-mélange pour la consolidation du sol (Grout Mixture for Ground Consolidation) Brevet d'invention No. 340,443 donnée au nom de la demanderesse (Patent No. 340,443 in the name of the applicant), Jan. 11, 1971; *Bulleten izobreteni*, No. 23, 1972

M. HAFFEN and J. JANIN

R. BARBEDETTE and G. LEENHARDT
Etanchements et consolidations (Waterproofing and Consolidation), *Techniques de l'Ingenieur*, C. 280-283, March 1972

J. WARNER

F.W. VINSON and J.K. MITCHELL

J.K. MITCHELL
Innovations in Ground Stabilization *ASCE Chicago Soil Mechanics Lecture Series, Innovations in Foundation Construction, March 1972*

K. MOLLER

A.R. ANDERSON (to J.J. Packo)
Stabilizing Soils *U.S.P. 3,660,984 - May 9, 1972*
72-09 A.J. WHITWORTH, S.Y. TUNG, E.A. HAJTO
Soil Grouting Process
U.S.P. 3,686,872 - Aug. 29, 1972

72-10 W. TOHMA, T. MURATA, W. NAHAMURA, A. KUDO
(to Sumitomo Durez Co., Ltd., Tokyo)
A Method of Soil Stabilization and Leakage Prevention

72-11 J. BOSSE
Contribution à l'étude des injections des sables très fins par le gel de silice. Thèse, Université de Nantes (Contribution to Research on the Use of Silica Gel for Grouting Very Fine Sands. Thesis)
July 27, 1972

72-12 H. NAVARRO, F. OTTMANN and J. BOSSE
Accès et intercommunications de la station Auber, phase V: Traitement confortatif des sables de Beauchamp par injection de gel de silice (Approaches and Connecting Tunnels in the Auber Station, Phase V: Reinforcement of Beauchamp Sand by Injections of Silica Gel), Travaux, Paris, No. 453, p. 9-24, Dec. 1972

72-13 H. NEUMANN and L.S. WILKINS
Soil Solidification by Chemical Injection
Civil Engineering and Public Works Review, p. 635, June 1972

72-14 C. CARON and J. GRANIER,
Coulis d'injection autoépaississant sous courant d'eau (Grout Which Thickens Automatically Under a Stream of Water)
F.P. 2,193,043 - July 24, 1972

72-15 C. CARON
Perfectionnement apporté aux gels d'étanchéité pour injection dans le sol (Improvements in Waterproofing Gels for Grouting Soils)
F.P. 2,195,239 - Aug. 3, 1972

73-01 A.S. FLATAN et al

228
73-02  BALLY et al
Consolidation of Soils and Making them Impermeable by Grouting with Rumanian Made Chemical Agents
Hydrotechnica, 18, No. 6, p. 295-302, 1973


73-04  V.E. SOKOLOVICH (URSS)
Proc. of the 8th Intern. Conf. on Soil Mechanics and Foundation Engrg., p. 351-352, Moscow, 1973

73-05  B.A. RZANITSYN (URSS)
ibid., p. 353-354, 1973

73-06  R. BARBEDETTE and P. FALCOZ
Sable très fin consolidé au silicate en site urbain (Very Fine Sand Consolidated with Silicate in an Urban Area), ibid., p. 378, 1973

73-07  V.F. DEMINE (URSS)
Réalisation des voiles d'injection dans les fondations sableuses à carbonates des barrages par l'injection des alcoylrésorçines (Grout Curtains Installed in the Carbonate-Type Sandy Foundations of Dams by Injections of Alcoylresorçins), ibid., p. 386, 1973

73-08  R.F. FOMICHEVA and A.K. BEKETOV
Silication of Loess Soils, ibid., p. 389, 1973

73-09  G. MIKI
Chemical Stabilization of Sandy Soils by Grouting in Japan, ibid., p. 395, 1973

73-11  G. MIKI
Chemical Soil Stabilization Recently Developed in Japan, SEISAN KENKYU - Monthly J. of Inst. of Industrial Sci., Univ. of Tokyo, Vol. 25, No. 8, p. 352-357, 1973

73-12  H.ASAO, T. HIHARA, S. ENDO, C. FURUYA, K. SANO
Soil Stabilization Method (to Toho Chem. Ind., Ltd.) U.S.P. 3,719,050 - March 6, 1973

229
Les fondements de l'amélioration artificielle des sols (Basic Principles of Artificial Soil Improvement), in Russian, 1973:
Chap. IV, p. 184, Emulsions bitumineuses (Bituminous Emulsions)
Chap. IV, p. 203, Stabilisation des sols à l'aide de polymères synthétiques (Soil Stabilization Using Synthetic Polymers)
Chap. IV, p. 233, Consolidation (Stabilization) des sols par lignosulfonates (Soil Consolidation (Stabilization) Using Lignosulfonates)
Chap. V, p. 238, Silicatation des sols (Soil Treatment with Silicates)

Procédé de traitement de terrains ou massifs poreux analogues par injection de coulis expansifs (Procedure for the Treatment of Ground and Similar Porous Masses by Injections of Expanding Grouts)
F.P. 2,230,209 - May 18, 1973


Dune Sand Stabilization with Synthetic Soil Conditioners: A Laboratory Experiment
Soil Science, 118, No. 5, p. 332-338, 1974

The Application of Chemical Grouts to Ground Consolidation, Ground Engineering, 7, No. 4, p. 42-44, 1974
BUTTNER

LOPEZ M.
Comments on Chemical Injections, Materiales Maquinaria y metodos para la Construccion, Valesquez, 105, Madrid 6, No. 112, p. 407-408, Spain, 1974

HALLIBURTON
Patents Pertaining to Grouting Soils for Water Shutoff or Consolidation, Patents List, 1974

J. WARNER

J.O. COTTA
Problemas de Inyeccion de subsuelos en areas urbanos (Problems with Grouting of Subsoil in Urban Areas), Conferencia XI Cursillo MC, Article published in the review MC, Dec. 1974

C. CARON, P. CATTIN and T. HERBST
Technique and Application of Injection in Granular Soil, Chapter 18, Foundation Engineering Handbook, Dr. H.F. Winterkorn and Dr. H.Y. Fang Edition, 1974


ROBERT BOWEN
Grouting in Engineering Applied Science Practice, Publishers 1975

LUONG, GANDAIS and ALLEMAND
<table>
<thead>
<tr>
<th>Ref</th>
<th>Author(s)</th>
<th>Title</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>76-02</td>
<td>A. GRAWITZ</td>
<td>Le Furfural: un nouvel essor (Furfural: A New Boom), Chimie Actualités (Chemical News), No. 1568, Feb. 11, 1976</td>
<td></td>
</tr>
<tr>
<td>76-03</td>
<td>H. CAMBEFORT</td>
<td>Eléments de rhéologie en mécanique des sols (Rheological Elements in Soil Mechanics), Annales ITBTP, March 1976</td>
<td></td>
</tr>
<tr>
<td>99-01</td>
<td>Terranier Grouting Process</td>
<td>Rayonier Inc., New York City</td>
<td></td>
</tr>
<tr>
<td>99-02</td>
<td>Alrem Soil Binder, Product Data, Pressure Grout Supply Co., Los Angeles, CA</td>
<td></td>
<td></td>
</tr>
<tr>
<td>99-03</td>
<td>Chemical Grout Field Manual, Engineering Chemicals Research Center, American Cyanamid Co., Princeton, NJ</td>
<td></td>
<td></td>
</tr>
<tr>
<td>99-04</td>
<td>AM-9 Chemical Grout, Technical Data, American Cyanamid Co., 1965</td>
<td></td>
<td></td>
</tr>
<tr>
<td>99-05</td>
<td>SIROC 132 (Instructions), Chemical Grout Laboratory Sample, SIROC DEPT., Raymond Concrete Pile Div., Raymond Intern. Inc., New York, NY</td>
<td></td>
<td></td>
</tr>
<tr>
<td>99-06</td>
<td>Superstruct 22-0 2, Product Data, Gra-Kote Chemical Coatings and Specialties, Northridge, CA</td>
<td></td>
<td></td>
</tr>
<tr>
<td>99-07</td>
<td>Les produits chimiques utilisables en injection des sols (Chemical Products Usable in Ground Grouting), Rhone-Poulenc, 1974</td>
<td></td>
<td></td>
</tr>
<tr>
<td>99-08</td>
<td>Takenaka's Aqua-Reactive Chemical Soil Stabilization System, Takenaka Komten Co., Tokyo, Japan</td>
<td></td>
<td></td>
</tr>
<tr>
<td>99-09</td>
<td>Durcisseur 600 (Hardener 600), Rhone-Progil</td>
<td></td>
<td></td>
</tr>
<tr>
<td>99-10</td>
<td>Sodium Silicate, Crossfield</td>
<td></td>
<td></td>
</tr>
<tr>
<td>99-11</td>
<td>Soil Treatment with PQ Co. Sodium Silicate, Philadelphia Quartz Co.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>99-12</td>
<td>Soil Solidification Sodium Silicate-Bicarbonate Method, Philadelphia Quartz Co.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>99-13</td>
<td>Rocagil 1295, Rhone Progil</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

99-15 Emploi de l'AM-9 (Use of AM-9), Documentation interne (Internal Documentation), Soletanche

99-16 Resins and Grouting Systems for Civil Engineering and Mining, Borden Ltd., U.K.

99-17 S.N.C.F. - Direction des Ouvrages d'Art (National Railroads) - Section for Bridges, Viaducts, Tunnels, Journées d'information Soletanche (Soletanche Information Journals), Quelques procédés nouveaux au stade Recherche et Développement (Some New Procedures Under Research and Development), Soletanche, Paris