

The tolerance on specific gravities determinations on standard 2-in. specimens is plus or minus 0.02. Assuming the same tolerance on large specimens it can be seen from the tables above that on a whole satisfactory test results are obtained using the modified gyratory molding procedure.

TABLE A

| | Specific Gravity (C-14, Test 5) | | |
|---------------------------------------|------------------------------------|------------------------------|----------------------|
| | Top $\frac{1}{2}$ | Middle $\frac{1}{2}$ | Bottom $\frac{1}{2}$ |
| 8-in spec. cut into 3 equal sections | 2.24 | 2.23 | 2.24 |
| 8-in. spec. cut into 2 equal sections | Top $\frac{1}{2}$ 2.22 | Bottom $\frac{1}{2}$ 2.21 | |

TABLE B

| Material | Specific Gravity (C 14, Test No. 5) | |
|---|--|------------|
| | 8 in. spec. | 2-in spec. |
| Dursey pit sand | 2.10 | 2.11 |
| Hartley Co. (1st run) | 2.20 | 2.20 |
| (2nd run) | 2.21 | 2.21 |
| Servtex (total mix) | 2.26 | 2.29 |
| Servtex coarse agg. Janes sand | 2.21 | 2.22 |
| Servtex coarse agg. Servtex dust Janes sand | 2.25 | 2.26 |
| Janes gravel ... Servtex dust | 2.32 | 2.33 |
| Janes gravel Janes sand | 2.26 | 2.29 |

METHYLCHLOROSILANES AS ANTISTRIPPING AGENTS

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SYNOPSIS

STRIPPING, a major source of failure in bituminous pavements, is caused by the displacement by water of the bituminous film on the surface and the resultant loss of adhesion between the aggregate particles. Although many techniques have been suggested to prevent stripping and subsequent pavement failures, none has met with outstanding success.

Stripping occurs most frequently when sandstone, chert, or any rock classified by geologists as acidic is used as aggregate. Limestone, dolomite, and the basic igneous rocks cause relatively little trouble. Unfortunately, limestone and the basic igneous rocks are not readily available in all localities where bituminous pavements must be constructed.

The siliceous rocks are hydrophilic, that is, water attracting, while limestone and the basic rocks are relatively hydrophobic. If an aggregate which is hydrophilic could be treated to make it hydrophobic, its resistance to stripping when coated with asphalt would be greatly improved.

This paper describes a method for coating a hydrophilic aggregate with a thin, tightly-bound film of silicone resin which will present a hydrophobic surface to the asphalt. The aggregate is exposed in a surface-moist condition to the vapor of a mixture of methylchlorosilanes, which react with the film of moisture on the aggregate to form a coating of silicone resin with a thickness of the order of a few hundred molecules. After exposure to the vapor, the aggregate is strongly hydrophobic.

In the laboratory, seven aggregates were investigated for stripping, with and without the silicone treatment. On the basis of three stripping tests, it was found that the performance of siliceous aggregates can be greatly improved by treatment with methylchlorosilanes.

● STRIPPING ACTION ordinarily begins at the bottom of the pavement and progresses gradually upward, its rate of progress being closely related to the density of the pavement. Therefore, the damage caused by stripping is

usually not apparent until after the pavement has failed over a large area.

Stripping is not frequent in the upper portion of the pavement for two reasons: first, because the wearing course is denser than the

subbase and is often protected from the action of surface moisture by a seal coat and, second, evaporation of any water which accumulates in the voids is more rapid in the upper than in the lower portion of the pavement.

There are many factors which influence the occurrence and rate of failure by stripping; among these are the amount of moisture present in the subgrade, the presence or absence of a seal coat, temperature, the chemical and physical properties of the bituminous binder, the amount of binder, and the nature of the aggregate. The last item is particularly important, because some minerals are hydrophobic and retain a bituminous coating in the presence of water, while others are hydrophilic and strip readily.

It is the purpose of this report to present

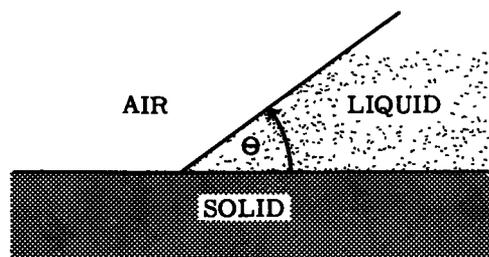


Figure 1.

experimental data showing that certain hydrophilic mineral aggregates can be made hydrophobic and their stripping characteristics greatly improved by treatment with organo-silicon compounds.

THEORY

A drop of any liquid placed on a solid surface behaves in one of two ways: it may remain as a drop, in the manner of a drop of water on a waxed surface, or it may spread out over the surface as water does on clean glass. If the drop spreads, the molecules of the liquid attract those of the solid more than they attract each other; quantitatively, the work of adhesion between the liquid and the solid is greater than the work of cohesion of the liquid itself. Mathematically, this relationship is expressed by Dupre's equation.

$$W_{SL} = \gamma_{SA} + \gamma_{LA} - \gamma_{SL} \quad (1)$$

where W_{SL} is the work of adhesion of the solid to the liquid, γ_{SA} and γ_{SL} are the surface ten-

sions of the solid against air and the liquid, and γ_{LA} is the surface tension of the liquid.

When a liquid rests on a solid, there is a definite angle θ at the solid-liquid interface called the angle of contact.

By treating the surface tensions as mathematical tensions parallel to the surfaces and resolving parallel to the solid surface, the following equation is obtained:

$$\gamma_{SA} = \gamma_{SL} + \gamma_{LA} \cos \theta \quad (2)$$

Combining equations (1) and (2) we have

$$W_{SL} = \gamma_{LA} (1 + \cos \theta) \quad (3)$$

It can be seen from equation (3) that the contact angle is determined by the relative

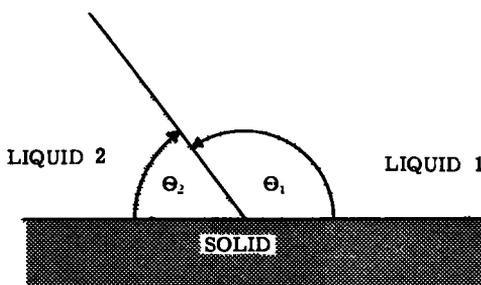


Figure 2.

strength of the adhesive force between the liquid and solid and the cohesive force within the liquid itself.

In the case of two liquids and a solid, *e.g.*, asphalt, water, and mineral aggregate, the mathematical treatment is similar and we arrive at the following expression:

$$W_{1S} - W_{2S} = \gamma_1 - \gamma_2 + \gamma_{1-2} \cos \theta_1 \quad (4)$$

where W_{1S} is the work of adhesion of the solid to Liquid 1, W_{2S} the work of adhesion of the solid to Liquid 2, γ_1 , the surface tension of Liquid 1 against air, and γ_2 the surface tension of Liquid 2 against air.

In general, a liquid which makes a small contact angle on a solid surface will tend to displace a liquid which makes a large contact angle. If asphalt makes a larger contact angle on the surface of a given aggregate than water, the asphalt will tend to strip.

The forces of adhesion and cohesion, and hence contact angles, are determined by intermolecular forces which are primarily electro-

static. If within a molecule of any substance the center of positive and negative charges does not coincide (which is usually the case), the molecule will behave as an electrostatic dipole and will orient itself in an electric field. Obviously two such molecules, if brought into proximity, will orient themselves with the center of positive charges of one molecule as closely as possible to the center of negative charges of the other; furthermore, work will be required to separate the two molecules.

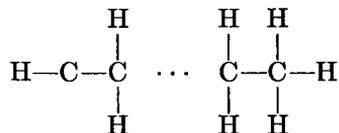
The magnitude of this dipole effect is a function of the total charge and the distance between the centers of positive and negative charge within the molecule and is often referred to as the dipole moment of the molecule. The molecular dipole moment varies greatly from substance to substance, that of water being comparatively high, while that of carbon tetrachloride or methane is zero. Saturated hydrocarbons have low dipole moments, the moments of most alcohols are intermediate, and those of organic acids are high.

The molecules of silica and most silicates have high dipole moments, higher than that of water molecules; therefore when a drop of water is placed on a clean sheet of glass or on a smooth quartz surface the drop spreads, since the force of attraction between the silica (or silicate) molecules and water molecules is greater than the force of attraction between two water molecules. Quartz, glass, and most silicates may properly be classed as hydrophilic substances. Carbonates of alkali-earth metals, *e.g.*, limestone, even though classed by the highway engineer as hydrophobic, are not non-polar substances; their molecules have a definite dipole moment much less than that of most siliceous materials but far greater than that of some other materials, *e.g.*, an unsaturated hydrocarbon such as paraffin wax. When compared with chert or glass, limestone is hydrophobic, but when compared with paraffin wax, limestone is hydrophilic.

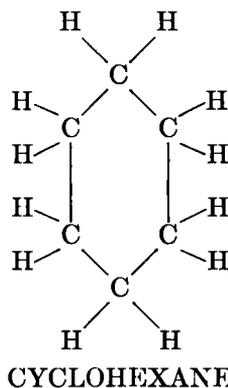
Asphalt, either natural or manufactured, is a mixture of various organic compounds which have been arbitrarily classified as: (1) *carboids*—that fraction of the asphalt which is insoluble in carbon disulfide; (2) *carbenes*—the fraction which is insoluble in carbon tetrachloride but soluble in carbon disulfide; (3) *asphaltenes*—which are soluble in carbon tetrachloride but insoluble in low boiling satu-

rated hydrocarbons; and (4) *maltenes*—which are soluble in low boiling saturated hydrocarbons such as octane (13). These constituents exist in asphalt in varying proportions as a colloidal mixture, the asphaltenes making up the major portion of the disperse phase, while the intermicellar phase consists primarily of the maltenes. Except in highly cracked or oxidized asphalts, the percentage of carbenes and carboids is very low.

About 35 to 60 percent of the compounds in the maltene group are saturated paraffinic compounds of the type shown below:



From 10 to 30 percent are alicyclic compounds of the cyclo-hexane type, and the balance of the maltene fraction



is made up of aromatic compounds either in aromatic structure or in various combinations with the paraffins and alicyclic compounds.

Little is known concerning the true nature of the asphaltenes. Analysis has shown, however, that they can be considered as "consisting of aromatic hydrocarbons containing paraffin chains to a varying extent, depending on the origin and manufacture of the bitumen" (13).

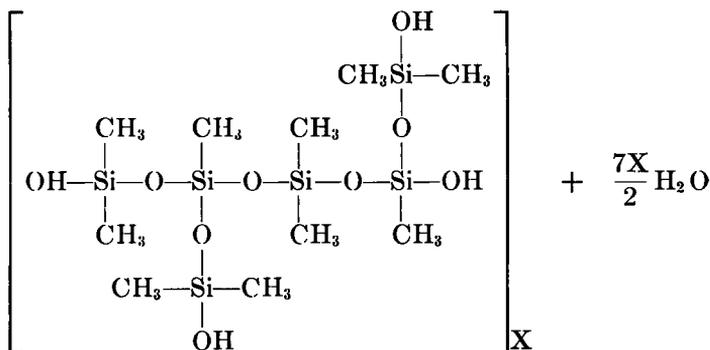
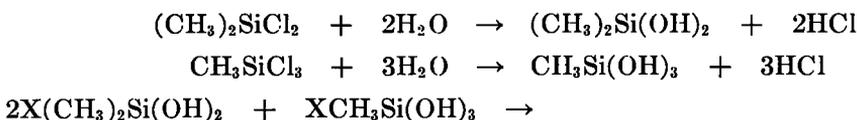
In general, the compounds found in asphalt have low dipole moments. Some organic compounds containing nitrogen and sulfur and most compounds containing a carboxyl or hydroxyl group are highly polar, but the percentages of these compounds in asphalt are

sandstone) with bituminous materials in the presence of water. He did not include any stripping tests in his experiments. As is to be expected from the chemistry of asphaltic materials discussed previously, McLeod also found that

for asphaltic materials from the same source and of equal viscosity, that asphaltic material having the largest percentage of asphaltenes plus carbenes has the greatest ability to displace water on the surfaces of the particles of a wet mineral aggregate.

The reason for this is evident since the complex aromatic compounds occurring in the asphaltenes and carbenes are more polar than the aliphatic paraffin-like compounds which constitute the greater proportion of the maltenes.

During World War II it was discovered that Steatite (ceramic) tube sockets, insulators, and other components used in electronic equipment can be made hydrophobic by exposing

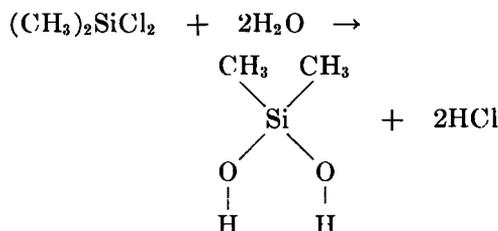


them for a short time in a surface-moist condition to the vapors of a mixture of chlorosilanes. This discovery has led to the use of many organosilicon compounds as waterproofing agents for various purposes. In the experiments described in this paper, a mixture of 66 $\frac{2}{3}$ % methyltrichlorosilane and 33 $\frac{1}{3}$ % dimethyldichlorosilane was used in an attempt to treat the surface of mineral aggregates.

Dimethyldichlorosilane and methyltrichlorosilane react with water to form complex oily or resinous polysiloxane compounds. The

reactions involved are extremely complex, and the final product formed depends on the temperature, the ratio of the two organosilicon compounds, the method by which they are brought into contact with water, and the rapidity with which the HCl liberated by the reaction is removed.

Dimethyldichlorosilane alone reacts with water in the following manner:



When a mixture of dichlorodimethylsilane and methyltrichlorosilane is hydrolyzed, co-condensation of the silanediols and silanetriols formed during hydrolysis occurs:

In a reaction of this type, the composition and physical properties of the final product are determined partially by the CH_3 to Si ratio in the original mixture of organosilicon halides. If the CH_3 to Si ratio is two or less, resinous products are formed which harden with age owing to further polymerization and co-condensation (14):

Methyl silicone polymers with CH_3 [to] Si ratios of 1.2, 1.3, 1.4, and 1.5 . . . are colorless solids with densities decreasing from 1.20 to 1.06; the time required to harden them at 100 C.

increases from two to 24 hours in the series. Below 1.2 methyl groups per silicon atom the resins are sticky syrups which cure at room temperature to hard, brittle glassy masses; above a ratio of 1.5, and particularly above 1.7, the products are oily and quite volatile, but set to a soft gel after several days or weeks at 200 C.

These methyl silicone polymers, or, more properly, polymethylsiloxanes, are highly stable (14):

As a group, the methyl silicone resins are characterized by excellent thermal stability and good resistance to oxidation. Samples have been heated to 550 C. *in vacuo* and to 500 C. in hydrogen without disintegration, decomposition, or melting; a transparent piece heated in air to 200 C. for one year looks the same as another piece of the same disk kept at room temperature. Above 300 C. the resins will oxidize slowly if they have free access to air, but for analytical combustions it has been found necessary to heat the samples to 550 C. or more in pure oxygen. The residue from oxidation under these conditions is a white mass of silica.

The methyl group has a very low dipole moment and is, therefore, strongly hydrophilic. When methylchlorosilanes react with the surface film of water which is found on most materials at ordinary conditions of temperature and humidity, hydrogen chloride is liberated and methyl-bearing silicon atoms are attached to the surface, thereby rendering the surface water repellent.

Both dimethyldichlorosilane and methyltrichlorosilane are volatile at room temperature. To treat any surface, it is necessary only to place the material to be treated in an enclosed chamber together with some of the silane mixture in an open vessel:

experimental facts point toward a hydrolytic reaction of methylchlorosilane vapor at the surface of the object being treated, depositing a thin film of methylpolysiloxane which becomes the water-repellent agent. . . . The important point is that the silicon atoms appear to be chemically [*sic*] bound to the substrate, probably through oxygen, and that they can be removed only by resorting to chemical action.

If it is assumed that the reaction follows the course which has been indicated, the organosilicon compound deposited by the reaction must be oriented with its oxygen bonds directly toward the substrate and its methyl groups extending outward from the surface. . . .

It is possible to draw some conclusions concerning the surface film from studies of the dimethylsiloxane molecule. The methyl groups

are about 3A apart, and the distance between chains is about 4A, and so the area of a single $(\text{CH}_3)_2\text{SiO}$ unit is . . . 21 square A. From Avogadro's number, one molecule of dimethyldichlorosilane should yield a monomolecular film 1.26×10^9 sq. cm. in area. Each gram of dimethyldichlorosilane should therefore cover an area of approximately 1,000 square meters with a single layer film. The thickness of such a film is about 6×10^{-8} cm.

Measurements which have been made on the water-repellent films themselves, as deposited on Steatite cylinders by vapor treatment allow some interesting comparisons with the calculated values. The gain of weight during the treatment of one cylinder was 1.9×10^{-5} grams per square centimeter; so that if the density is taken as 1.0, the film must be 1.9×10^{-5} cm. thick. If it is assumed that the previously calculated thickness of a monolayer is correct, this particular film must have been . . . about 300 molecules thick. This is the same order of magnitude as the number of water molecules piled one upon another in the adsorbed film on silica at high humidities, so that, if Steatite has approximately the same kind of adsorbed film as silica, the methylchlorosilane reacts molecule for molecule with the water film. The entire water film therefore is replaced by one of methyl silicone.

Theoretically, any mineral aggregate could be coated with a silicone film by treatment with methylchlorosilane vapor. The aggregate would then become strongly hydrophobic; it could easily be coated with asphalt in the presence of water, and the coated aggregate would not strip readily. This treatment would have an important advantage over that described by McLeod in that the quantities of "silicone" materials do not have to be closely controlled. In the treatment described by McLeod, the quantities of both collecting and activating agents must be maintained within quite narrow limits, otherwise the aggregate will not be made hydrophobic. Although this is easily accomplished under laboratory conditions, it would be difficult to control accurately the amounts of these chemicals used in practice. Furthermore, the quantities of activating and collecting agents which should be used vary markedly with the mineralogical and chemical composition of the rock. Therefore, in the case of a glacial gravel which is composed of different rocks of widely varying chemical composition, the treatment outlined by McLeod might not be entirely successful.

Treatment of aggregates with silanes would not have this disadvantage. If enough of the methylchlorosilane mixture is present to re-

act completely with the surface film of moisture, an excess will cause no difficulty.

EXPERIMENTAL PROCEDURES

In the tests described in the following pages, seven mineral aggregates were chosen as representative of the constituents, chemi-

and a measured amount of two-thirds methyl-trichlorosilane and one-third dimethyldichlorosilane was poured into a shallow, open vessel inside the box. The lid was placed securely on the box, and sufficient time was allowed to elapse before the aggregate was removed. During treatment, the cylindrical

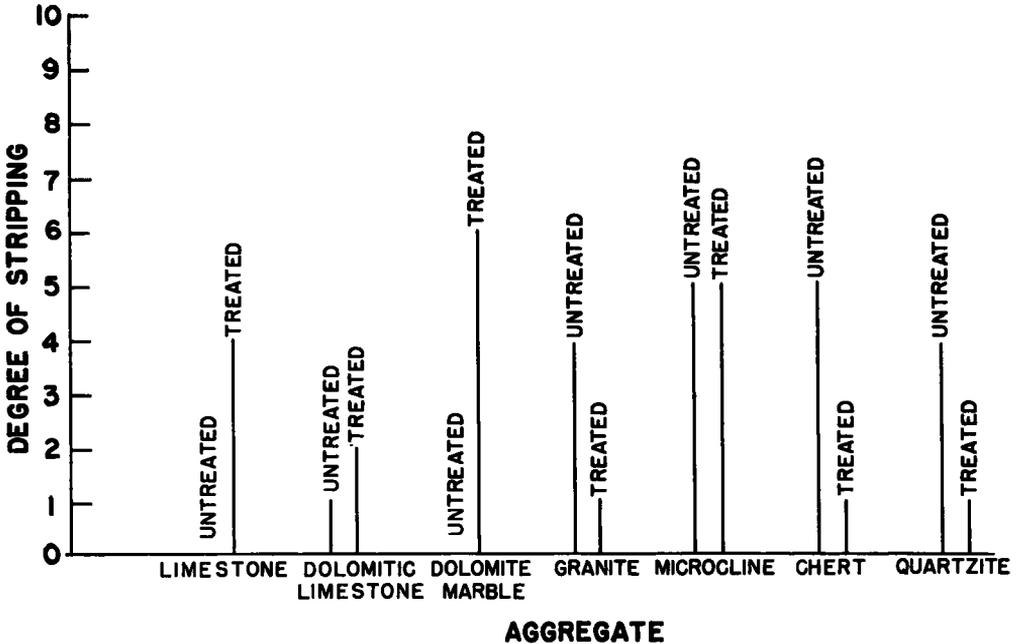


Figure 3. Tyler wash test: degree of stripping from untreated and treated aggregates.

cally speaking, of aggregates used commonly for road building. These aggregates were as follows:

- | | |
|------------------------|------------------------------------|
| 1. Limestone | Onondaga County, New York |
| 2. Dolomitic limestone | Rochester, New York |
| 3. Dolomite marble | Lee, Massachusetts |
| 4. Biotite granite | Woodbury, Vermont |
| 5. Quartzite | Dell Rapids, South Dakota |
| 6. Chert | Joplin, Missouri |
| 7. Microcline | Parry Sound Dist., Ontario, Canada |

Obviously no highway engineer, except under very unusual circumstances, would use microcline or chert as an aggregate for constructing a wearing course or even a subgrade. However, these minerals are commonly found in many rocks used for highway construction.

The minerals and rocks to be tested were exposed to the silane vapor in a specially constructed closed box fitted with a cylindrical screen which could be rotated by a crank. The aggregate was placed inside this screen

and a measured amount of two-thirds methyl-trichlorosilane and one-third dimethyldichlorosilane was poured into a shallow, open vessel inside the box. The lid was placed securely on the box, and sufficient time was allowed to elapse before the aggregate was removed. During treatment, the cylindrical

screen was rotated occasionally to insure that all aggregate surfaces would be exposed to the vapor. Before treatment with the methylchlorosilane mixture, the aggregate was stored in a moist cabinet for 30 min. so that the surface moisture film on the aggregate would be approximately the same thickness on different days regardless of room temperature and humidity.

Fifty milliliters of the methylchlorosilane mixture were used for each kilogram of coarse aggregate. This is many times the amount theoretically necessary, but it was thought that it would be desirable to make ample allowance for moisture on the inside of the box and on the screen which would react with the vapor, and for the escape of vapor through joints in the box.

After treatment it could be observed that

the contact angle of water on the surface of the treated aggregate was so great that water stood in small drops on the surface, and a small piece of treated aggregate immersed in water was surrounded by a film of air.

Tyler Wash Test—For this test, described completely by Tyler (17), a 500-gram sample of each aggregate under consideration was coated with 5 percent by weight of Socony MC-2 cutback asphalt. After a seven-day curing period, the coated aggregate was separated into particles and placed in a jar with

TABLE 1
TYLER WASH TEST DEGREE OF STRIPPING
FROM UNTREATED AND TREATED
AGGREGATES

| Rock or mineral | Untreated degree of stripping | Treated degree of stripping |
|---------------------|-------------------------------|-----------------------------|
| Limestone | 0 | 4 |
| Dolomitic limestone | 1 | 2 |
| Dolomite marble | 0 | 6 |
| Granite | 4 | 1 |
| Quartzite | 4 | 1 |
| Microcline | 5 | 5 |
| Chert | 5 | 1 |

TABLE 2
SODIUM CARBONATE SOLUTIONS FOR
RIEDEL-WEBER TEST

| Solution No. | Concentration | Sodium carbonate |
|--------------|------------------------------|------------------------|
| | <i>molar</i> (pure water) | <i>grams per liter</i> |
| 0 | | 0 |
| 1 | 1/265 | 0.414 |
| 2 | 1/128 | 0.828 |
| 3 | 1/64 | 1.657 |
| 4 | 1/32 | 3.313 |
| 5 | 1/16 | 6.625 |

one liter of distilled water at room temperature. The jar was then placed in a rack built to fit into a Ro-tap machine and shaken for 30 min. The aggregate was removed from the jar, allowed to dry, and rated for stripping on a ten-point scale. On this scale, 0 denotes no stripping, 1 to 3 slight stripping, 4 to 7 moderate stripping, and 8 to 10 excessive stripping. Table 1 gives average values based on the ratings of three observers.

On the basis of the Tyler wash test alone, it would appear that stripping from the siliceous aggregates, chert, granite, and quartzite is inhibited by treatment with the methylchlorosilane vapor. Stripping from the non-siliceous aggregates appears to have been increased by treatment.

Riedel-Weber Test (Modified)—For this test, several pieces approximately 1 in. in size of each mineral to be tested were treated with the methylchlorosilane vapor, washed thoroughly, and placed in an oven for 24 hr. at 100 C. They were then coated with 5 percent by weight of Socony RC-0 cutback asphalt. The coated aggregate was allowed to cure for 24 hr.

Five solutions of increasing concentration were made up of sodium carbonate. The concentration of each solution is given in Table 2.

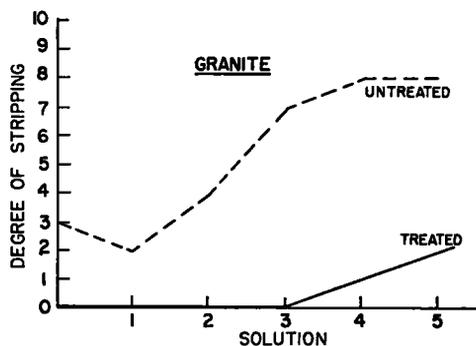
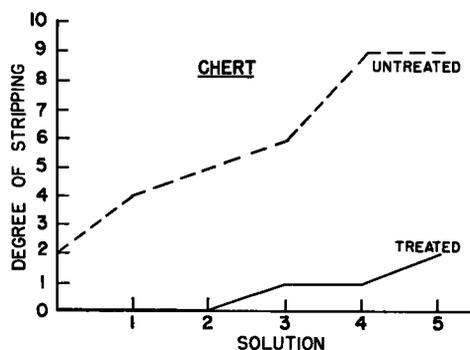


Figure 4. Riedel-Weber test: degree of stripping from treated and untreated aggregates.

Several pieces of each aggregate, both treated and untreated, were boiled in a solution for 1 min. and then removed and allowed to dry. This process was repeated for each solution, using different pieces of aggregate. After drying, the specimens were inspected for stripping and rated on the same ten-point scale used in the Tyler test.

According to the results obtained on the Riedel-Weber test, stripping of the bituminous film from all the aggregates tested was retarded by treatment of the aggregate with

methylchlorosilanes. The inhibition of stripping was much more pronounced with the siliceous rocks than with the carbonate rocks. The stripping values given in Table 3 are average values based on the ratings of nine observers.

Immersion-Compression Test—Within recent years this test has been described so fre-

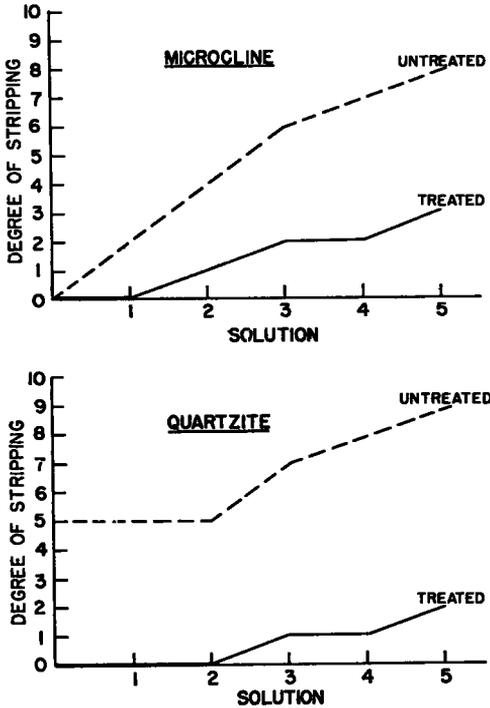


Figure 5. Riedel-Weber test: degree of stripping from treated and untreated aggregates.

quently in technical journals that a detailed discussion of the procedure does not seem necessary. The test is described completely in *ASTM Standards 1949*, Part 3. (2, p. 1026 ff., p. 1052 ff., ASTM D 1074-49T and D 1075-49T).

The minerals to be tested were crushed and screened so that the fraction used in the test passed the $\frac{1}{2}$ -in. sieve and was retained on the $\frac{1}{4}$ -in. sieve. After crushing and screening, half of the aggregate to be tested was treated with methylchlorosilane vapor. The treated aggregate was washed and placed in an oven at 100 C. for 24 hr. as in the Riedel-Weber test.

Each aggregate to be tested was combined

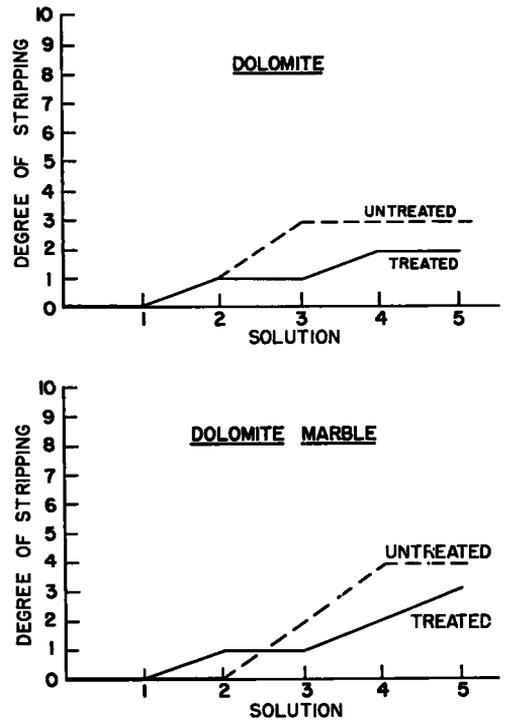


Figure 6. Riedel-Weber test: degree of stripping from treated and untreated aggregates.

with that quantity of Ottawa sand which would give theoretical maximum density. The mixture of coarse and fine aggregate was brought to a temperature of 325 F., and 7.0 percent by weight of Socony 85-100 penetration asphalt cement was added. For the tests on sand alone, the percentage of asphalt was increased to 9.5 percent by weight. After

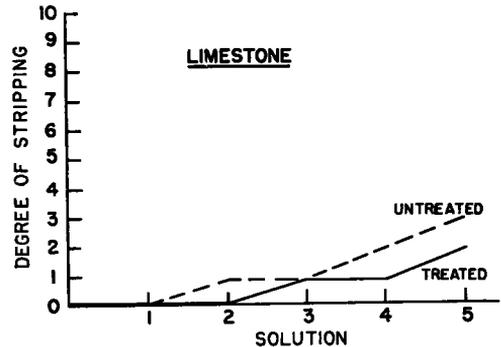


Figure 7. Riedel-Weber test: degree of stripping from treated and untreated aggregates.

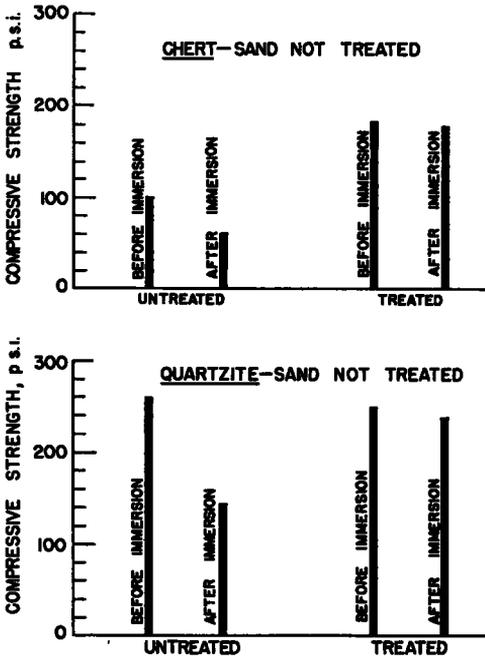


Figure 8. Immersion-compression test: compressive strength test specimens.

Twelve cylinders were molded for each mineral or rock; six with untreated and six with treated aggregate. Tests were also made on the Ottawa sand used as fine aggregate, both treated and untreated. Except in the case of chert, where six extra cylinders were made, the sand used as fine aggregate was not treated.

After curing, the cylinders were divided into groups of three on the basis of bulk specific gravity and tested as described in ASTM D 1075-49T. Six cylinders made with each aggregate, three treated and three untreated, were tested in unconfined compression immediately after curing. The remaining six cylinders were placed in a constant temperature water bath at 49 C. for four days, after which they were tested in unconfined compression.

Because of the varying elastic constants, etc. of the different rocks and minerals, the grading between the 1/2-in. and 3/4-in. limits was probably different for each aggregate. Although this makes no difference in a comparison of treated versus untreated samples of the same aggregate, a comparison of different aggre-

TABLE 3

RIEDEL-WEBER TEST—DEGREE OF STRIPPING AFTER BOILING FOR ONE MINUTE IN SOLUTIONS INDICATED

| Material | Solution number | | | | | |
|------------------------|-----------------|---|---|---|---|---|
| | 0 | 1 | 2 | 3 | 4 | 5 |
| <i>Dolomite</i> | | | | | | |
| Untreated | 0 | 0 | 1 | 3 | 3 | 3 |
| Treated | 0 | 0 | 1 | 1 | 2 | 2 |
| <i>Dolomite Marble</i> | | | | | | |
| Untreated | 0 | 0 | 0 | 2 | 4 | 4 |
| Treated | 0 | 0 | 1 | 1 | 2 | 3 |
| <i>Chert</i> | | | | | | |
| Untreated | 2 | 4 | 5 | 6 | 9 | 9 |
| Treated | 0 | 0 | 0 | 1 | 1 | 2 |
| <i>Granite</i> | | | | | | |
| Untreated | 3 | 2 | 4 | 7 | 8 | 8 |
| Treated | 0 | 0 | 0 | 0 | 1 | 2 |
| <i>Microcline</i> | | | | | | |
| Untreated | 0 | 2 | 4 | 6 | 7 | 8 |
| Treated | 0 | 0 | 1 | 2 | 2 | 3 |
| <i>Limestone</i> | | | | | | |
| Untreated | 0 | 0 | 1 | 1 | 2 | 3 |
| Treated | 0 | 0 | 0 | 1 | 1 | 2 |
| <i>Quartzite</i> | | | | | | |
| Untreated | 5 | 5 | 5 | 7 | 8 | 9 |
| Treated | 0 | 0 | 1 | 1 | 2 | 2 |

mixing, cylindrical specimens were molded as described in *ASTM Standards*.

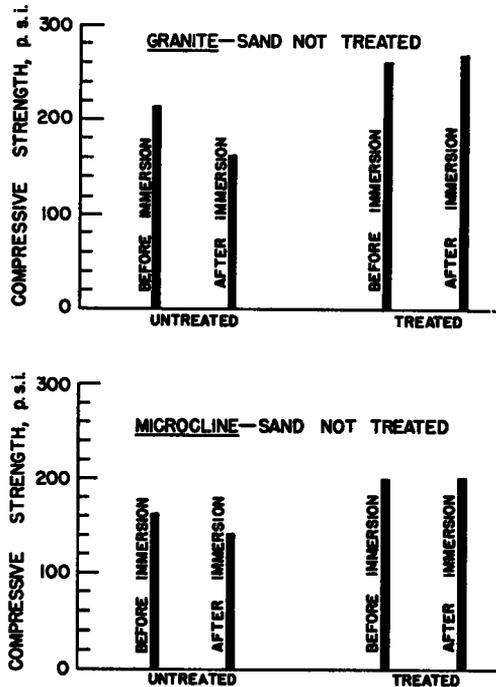


Figure 9. Immersion-compression test: compressive strengths of test specimens.

gates on the basis of this test would not be valid.

The results of the immersion-compression test are summarized in Table 4.

the Tyler wash test indicated that stripping from the carbonate rocks, dolomitic limestone,

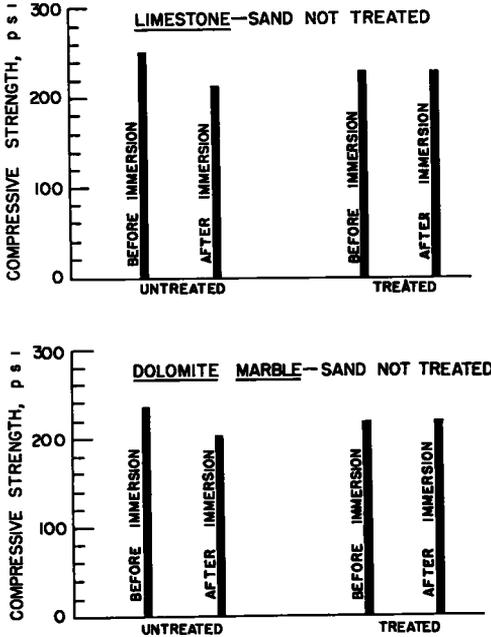


Figure 10. Immersion-compression test: compressive strengths of test specimens.

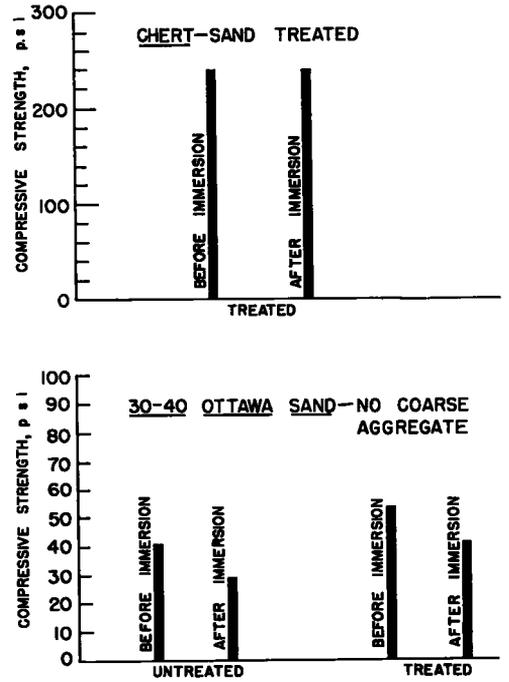


Figure 11. Immersion-compression test: compressive strengths of test specimens.

TABLE 4
IMMERSION-COMPRESSION TEST—STRENGTH OF CYLINDERS MADE WITH TREATED AND UNTREATED AGGREGATES

| Aggregate | Untreated | | | Treated | | |
|------------------------------|---------------------------|--------------------------|--|---------------------------|--------------------------|--|
| | Strength before immersion | Strength after immersion | Percentage of original strength retained | Strength before immersion | Strength after immersion | Percentage of original strength retained |
| | psi. | psi. | percent | psi. | psi. | percent |
| Chert ^a | 103 | 64 | 62 | 183 | 179 | 98 |
| Quartzite ^a | 262 | 143 | 54 | 254 | 238 | 94 |
| Granite ^a | 214 | 166 | 78 | 262 | 270 | 103 |
| Microcline ^a | 159 | 143 | 90 | 206 | 206 | 100 |
| Limestone ^a | 246 | 214 | 88 | 222 | 222 | 100 |
| Dolomite marble ^a | 238 | 206 | 87 | 222 | 222 | 100 |
| Ottawa sand (30-40) | 40 | 28 | 69 | 52 | 40 | 78 |
| Chert (sand also treated) | — | — | — | 238 | 238 | 100 |

^a Ottawa sand used as fine aggregate not treated with methylchlorosilanes.

REVIEW AND ANALYSIS

According to the results obtained on the Riedel-Weber test and the immersion-compression test, stripping from all the aggregates was inhibited by treatment with the methylchlorosilane mixture. The results of

limestone, and dolomite marble was increased by the silicone treatment. The results of the Tyler test on the siliceous rocks, granite, quartzite, microcline, and chert showed that stripping was retarded by the treatment.

It was thought that the poor performance

of the carbonate rocks in the Tyler test might be caused by either or both of the following factors: (1) the formation of calcium or magnesium chloride by the reaction of HCl with the carbonate rock and (2) incomplete polymerization and incomplete co-condensation of the silicone film. Calcium chloride and magnesium chloride are highly polar, and the presence of even a very small quantity of either of these substances on the surface of the aggregate would cause an increase of stripping.

In order to determine whether or not this was the case, the Tyler wash test was repeated on dolomite marble. After treatment with the methylchlorosilane vapor, the aggregate was washed thoroughly to remove any HCl, CaCl₂, or MgCl₂ which might remain on the surface. The aggregate was then placed in an oven at 100 C. for 24 hr. to cure the silicone film. The anti-stripping properties of the silicone film were apparently greatly improved by washing and heat treatment. After 30 minutes' agitation with distilled water, the treated sample showed only very slight stripping: 0.5 on the ten-point scale.

The outcome of this experiment was not investigated further, because of lack of time. However, the aggregates used in the Riedel-Weber test and the immersion-compression test were washed thoroughly and kept at a temperature of 100 C. for 24 hr. after treatment with the methylchlorosilane vapor.

None of the stripping tests published to date is entirely satisfactory, and the three tests used in these experiments suffer from many disadvantages. The Tyler test does not simulate road conditions. The particles of aggregate are agitated violently in a jar of water, and it would seem that most of the stripping which occurs is caused by mutual abrasion of the aggregate particles. The conditions of the Riedel-Weber test are even further removed from those actually found in a bituminous pavement. In the hottest climates, a pavement surface seldom reaches a temperature greater than 140 F., and the high concentrations of OH⁻ ions in the sodium carbonate solutions are not found in any pavement.

In devising the immersion-compression test, an attempt was made to eliminate these faults. The temperature of the immersion bath is kept at 49 C. and the compression tests are

carried out at 77 F. These temperatures are well within the limits of those which actually occur in highway pavements. It seems doubtful, however, that a pavement ever fails in unconfined compression. A triaxial-compression test would probably be a closer approximation.

The immersion-compression test is long, involved, and requires special apparatus not usually found in a highway engineering laboratory. The results of the test are somewhat dubious, even when performed with the best laboratory equipment. The addition of an automatic-loading device to control the rate of deformation of the bituminous cylinders during compression would greatly increase the accuracy of the results.

CONCLUSIONS

1. Data obtained from the three stripping tests performed in the laboratory indicate that the tendency of asphalt films to strip from the aggregates tested can be reduced by treatment of the aggregate with methylchlorosilanes. As is to be expected, the improvement is very great with the siliceous aggregates which are usually classed as hydrophilic. The antistripping properties of treated aggregates containing carbonate rocks can apparently be increased by washing the aggregate and curing it at 100 C. for 24 hr. after treatment.

2. None of the presently used stripping tests is satisfactory. It might be possible to predict stripping more accurately by studying the contact angles formed by water and asphalt on the surface of the aggregate.

3. In order to determine the practical value of the methylchlorosilane treatment, it will be necessary to construct test strips of highway using treated aggregate.

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RATE OF COOLING OF LAVA FLOWS

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SYNOPSIS

The massive Mauna Loa lava flow of June 1950 buried about a mile of the main-belt highway on the Island of Hawaii to depths up to 60 ft. The initial temperature of the lava as it crossed the road was 950 C. Heat loss by thermal radiation from the surface was of importance only during the initial period of a few weeks. Thereafter the rate of cooling became dependent on the rate of heat conduction from the interior to the surface. Computations of temperatures at different depths for various periods of cooling from $\frac{1}{2}$ yr. to 5 yr. were made by the theory of heat conduction. The study showed that at the depths of cut proposed in reconstructing the highway, the cooling rate was extremely slow, so that a prolonged period of waiting would probably be necessary. This conclusion seems supported, at least in a qualitative way, by comparative temperatures at depths of 18 in. or so within cracks in the lava taken 5 months (November 1950) and 15 months (September 1951) after the flow ceased. The measurements revealed only a slight drop in temperature in the colder cracks (250 F) and practically none in