

APPLICATIONS OF SURFACE CHEMISTRY AND PHYSICS
TO BITUMINOUS MIXTURES

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In presenting this rather theoretical paper, the writer is perfectly aware that the various concepts or theories advanced to explain the experimental results so far obtained, and the conclusions reached, tentative and otherwise, may have to be amended as more data are accumulated. The whole history of scientific discovery makes this almost inevitable. The theories presented, however, are quite well substantiated by research data so far obtained, and should serve as a starting point for the more intensive research in this rather promising field which it is hoped the paper will stimulate.

Every endeavor, consistent with reasonable brevity, has been made to present the material as simply as possible, since few engineers, outside of certain fields, have found it necessary to make any special study of chemistry and physics.

PART I*

THE COATING OF WET MINERAL AGGREGATES
WITH BITUMINOUS MATERIALS

The experimental results presented in Part I of this paper were obtained by the writer over a period of several years largely in the Chemical Laboratory at the University of Saskatchewan, but partly in the Testing Laboratory of the Saskatchewan Highway Department.

The writer wishes to gratefully acknowledge his indebtedness to Dr. T. Thorvaldson, Head of the Department of Chemistry at the University of Saskatchewan, under whose general direction this research was carried out, for the many hours he so freely gave to stimulating discussion.

Introduction

At the present time, the coating of mineral aggregates with bituminous materials for the surfacing of highways and airports, and for other engineering purposes, can in general only be successfully accomplished when the surfaces of the aggregate particles are dry. While the use of bituminous emulsions permits the coating of wet aggregates, for various reasons they have not been universally adopted.

*Part I of this paper is condensed from a thesis presented to the Graduate School of the University of Saskatchewan in partial fulfillment of the requirements for the degree of Master of Science in September, 1936.

The necessity for drying the aggregate results in expensive delays after rains if the aggregates and bituminous materials are being mixed in place, and involves the use of somewhat expensive drying equipment in all modern stationary asphalt paving plants. On small projects, the transportation and operating costs of these driers are appreciable items in the ultimate cost of the finished road surface.

In recent years asphalt paving technologists have been considerably perturbed because many aggregates have a greater adhesion tension for water than for bituminous materials. Since an aggregate tends to become coated by the liquid present for which it has the greatest adhesion tension, water tends to strip the bitumen from the aggregate in many bituminous surfaces constructed at the present time, resulting in shorter life and higher maintenance costs.

If it were possible to change the surface characteristics of the aggregate particles so that they had a greater adhesion tension for bituminous materials than for water, bituminous surfaces could be constructed which were thermodynamically stable in the presence of water. With such a change in the surface characteristics of the particles, there would be no necessity for a drier since the bituminous materials would completely displace the water on the surfaces of damp or wet aggregates even in the presence of a large excess of water. The necessity for a drier, as a drier, would be entirely eliminated, although it might be desirable to retain it in the capacity of a heater for the aggregate to permit the use of higher consistency bitumens. However, modern developments in the use of cut-backs, powdered asphalts, etc., would make it possible to eliminate any necessity for even heating the aggregate.

It is the purpose of Part I of this paper to show that the required changes in the surface characteristics of mineral aggregates for these purposes can be accomplished simply and economically, for many aggregates at least, by the use of certain chemical reagents.

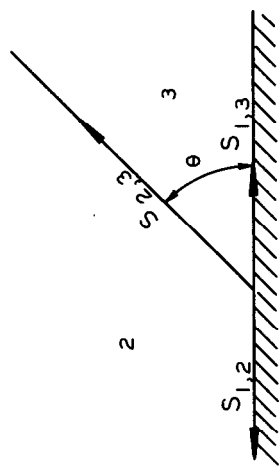
Theoretical Background

The surface energy equations involved when one immiscible liquid displaces another on the surface of a solid, or vice versa, can be found in any textbook on surface chemistry or physics.

If a solid surface has a greater adhesion tension for water than for an organic liquid (Fig. 1), the following equation must hold:

$$A_{1,3} - A_{1,2} = S_{1,2} - S_{1,3} \quad (1)$$

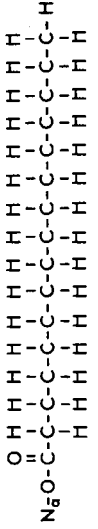
where A = adhesion tension, which is a measure of the attraction between a solid and a liquid, expressed as dynes/cm or ergs/cm²;



$$A_{1,3}^{-1} A_{1,2} = S_{1,2}^{-1} S_{1,3}$$

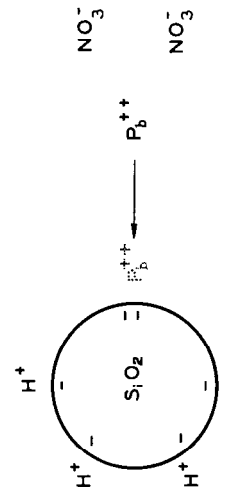
SOLID-LIQUID SURFACE ENERGY RELATIONSHIPS

FIGURE 1



SODIUM PALMITATE - A SOAP USED AS
A FLOTATION COLLECTING AGENT.

FIGURE 2



ACTION OF LEAD NITRATE AS AN ACTIVATING AGENT.

FIGURE 3

S = interfacial tension, which is a measure of the repulsion between a solid and a liquid, expressed as dynes/cm or ergs/cm²;

and the subscripts 1, 2, and 3 refer to solid, organic liquid, and water respectively.

In words, Eq. (1) states that the adhesion tension between a solid and an organic liquid ($A_{1,2}$) is less than the adhesion tension between the same solid and water ($A_{1,3}$), if the interfacial tension between the solid and water ($S_{1,3}$) is less than the interfacial tension between the solid and the organic liquid ($S_{1,2}$). It also states that the difference between these two adhesion tensions is numerically equal to the difference between the two interfacial tensions.

The minerals composing ordinary aggregates are chiefly carbonates of calcium and magnesium, silicon dioxide, and complex silicates of potassium, sodium, calcium, aluminum, iron, etc. These are all polar minerals (possess dipole moments), and have a high attraction for water (high $A_{1,3}$) a highly polar liquid, and a low attraction for organic liquids (low $A_{1,2}$) which are non-polar.

Consequently, it is necessary to change the surface characteristics of the particles of an aggregate to make the attraction between these and organic liquids ($A_{1,2}$) high, and their attraction for water ($A_{1,3}$) low, if bituminous materials are to displace water on the surfaces of wet aggregates in the absence of an emulsification action.

To bring about such an alteration in the properties of the surfaces of mineral aggregates, certain chemical reagents must be used. These chemical reagents must be of such composition as to give the mineral surfaces a high repulsion for water (high $S_{1,3}$ or low $A_{1,3}$), and at the same time a high attraction for bituminous materials (low $S_{1,2}$ or high $A_{1,2}$).

An examination of industrial fields in which wetting agents are employed, and of the theory behind the use of wetting agents in each field, revealed that a large amount of useful data as to possible reagents and reaction conditions for successfully attacking this problem might be furnished by the flotation processes employed in the ore dressing of minerals.

In many ore flotation processes, the changing of the surface characteristics of mineral particles by means of chemical reagents to make them temporarily or permanently lyophilic (fluid attracting), or lyophobic (fluid repelling) to water as operating conditions demand, is a commonplace occurrence. The surface of a mineral particle must be lyophobic towards water before the mineral particle can become attached to an air bubble and be lifted from the flotation pulp.

The whole purpose of the collecting agents (wetting agents), xanthates, thiocarbamides, thiophosphates, fatty acids, soaps, etc., used in flotation processes, is in general to secure a water-repellent, water-insoluble, surface film on the mineral particle, generally through the reaction of the collecting agent with metallic ions on the surface of the particle. The hydrocarbon ends of the collector molecules (Fig. 2) are oriented outward from the surface of the mineral particle to be floated, presenting essentially a hydrocarbon surface to the water, repelling water, and at the same time attracting the air present in flotation systems. These collecting agents therefore, upon being adsorbed on a mineral surface, make the particle behave as though it had been coated with a very thin greasy film, or more correctly possibly, flecked with very small grease spots.

If a similar water-repellent film, created by the use of similar reagents, could be formed on the surfaces of mineral aggregates used in bituminous mixtures, the conditions would be created whereby bituminous materials would displace water from the surfaces of wet mineral aggregates even in the presence of a large excess of water, since bitumens, being oily materials, would have a high adhesion tension for such a water-repellent surface.

Furthermore, since the aggregate so conditioned would have a greater adhesion tension for bituminous materials than for water, bituminous mixtures made with such aggregates would be stable against any uncoating tendency of water.

However, since a flotation system is made up of the three phases solid-water-air, while the system of the bituminous mixtures being considered is made up of the three phases solid-water-bitumen, there are a number of physico-chemical reasons why the reagents and reaction conditions used in ore flotation processes cannot be used in toto for the purpose of causing bituminous materials to displace water on the surfaces of wet mineral aggregates. These reasons will be evident from the material presented in the following pages to any one familiar with the present status of flotation theory, and are largely due to the fact that in the latter system there are two immiscible solvents present, one polar (water), the other essentially non-polar (bitumen), while in a flotation system water is essentially the only solvent medium present.

In the art of flotation, in addition to collecting agents (wetting agents), it has been found necessary for recovering some minerals, to use other reagents called activating agents. The function of these can best be illustrated by an example.

Collecting agents such as soaps, cannot bring about a material flotation of pure crushed quartz,

since soaps cannot form a water insoluble, water-repelling compound with any constituent present in a pure quartz surface. Quartz, however, will adsorb heavy metal and alkali earth metal cations such as lead, copper, iron, calcium, etc., from solutions of salts of these. These adsorbed metallic ions in turn will react with the fatty acid radicals of soaps, forming a water-insoluble, water-repellent, soap film on the surface of a quartz particle to which an air bubble can become attached to bring about its flotation.

Salts of metallic ions which function in this manner are called activating agents.

In Fig. 3 the activation of a particle of silica gel by lead nitrate as a base exchange reaction is illustrated. While the actual mechanism of the activation of the surfaces of particles of crushed quartz is not yet agreed upon by flotation research workers (10), it is not unlikely that this is also a base exchange reaction (11).

From a study made at the beginning of this investigation of the functions and properties of activating and collecting agents as given in flotation literature, it appeared likely that for the displacement of water on the surfaces of wet mineral aggregates by bituminous materials, any metallic cation in the periodic table which could be adsorbed by the mineral aggregate being investigated, and would give an insoluble compound with some wetting agent, could function as an activating agent, and any organic compound containing a water-repellent hydrocarbon grouping, and capable of forming an insoluble compound with a metallic ion on the surface of a mineral particle, could function as a wetting agent.

With the object of testing this possibility, many hundreds of experimental mixtures of wet mineral aggregates, bitumen, and reagents were made up and studied. Almost every metallic ion was tried out as activating agent, and a considerable number of organic compounds were used as wetting agents. Some of the results are tabulated in the following tables.

While the commonest aggregates for bituminous mixtures are natural sands and gravels, crushed stone, and slag, these are of such variable composition mineralogically that it was deemed advisable to limit the aggregate to one mineral or one rock in each case at first, and study the possibilities for commercial aggregates later. Tables 1 to 5, therefore, contain data for one mineral or one rock in each case. The aggregates for the remaining tables, where these concern aggregates, are sands from commercial gravels.

Experimental Procedure

The following experimental procedure was adopted throughout for these mixtures except where specifically stated to be otherwise.

Thirty (30) grams of the mineral aggregate being studied, passing a No. 8 sieve, retained on a No. 40 sieve, were weighed and placed in a 150 cc beaker. Enough distilled water was added to cover the aggregate in the bottom of the beaker, and all water drained off which was not retained by the mineral particles. About 8 to 10 grams of water were retained by the aggregate after draining. One gram of bituminous oil was added to the wet aggregate. By means of pipettes, small quantities of solutions of activating agent, wetting agent, or other reagents were added. Mixing was done with a horn spatula because of its chemical inertness, and with a stirring motion.

Since there are various degrees of perfection for the coating of wet aggregates with bituminous materials obtained through the use of these reagents, the degree of perfection increasing within limits as more of the reagents are added, it was found advisable to use a standard mix for each aggregate in order to quantitatively compare the quantities of reagents required to give a certain standard perfection of coating.

The least quantity of either lead or copper ions as activating agent, and of soap as wetting agent, which would just bring about complete coating of each wet aggregate, was observed. This mixture served as the standard for that aggregate. The amounts of other reagent combinations required to give as good a coating as that of the standard were then determined.

Lead or copper ions were used as activating agent for the standard since in general these are the most satisfactory activating agents. The procedure for determining the quantities of each reagent required was as follows:

One reagent was added in small quantities, usually a fraction of a cubic centimeter at a time, until the further addition was without noticeable effect, when small quantities of the other type of reagent were added until it was without effect, the mixture being thoroughly stirred after each addition. This was repeated until a coating as good as the standard was obtained or until it became evident that complete coating could not be obtained with the reagent combination being used.

The metal salts used as activating agents were all labeled chemically pure. The sodium oleate which was used very largely as a wetting agent was of technical grade. There was no necessity for further purification of these materials for this investigation.

All activating agent and wetting agent solutions were 0.05 Molar in the ion or radical being investigated.

Distilled water which gave no precipitate with sodium oleate solution was used throughout.

The bitumen used, except where specifically stated to be otherwise, was a non-volatile, cracking-coil product. Some of its characteristics are given in table 10, where it is the first bitumen listed.

It should be pointed out here that when using a 30-gram sample of aggregate, each cubic centimeter of sodium oleate and lead nitrate solutions, the most generally used reagents, corresponds to approximately one pound of each reagent per ton of aggregate.

Experimental Results and Discussion

Tables 1, 2 and 3 are practically self-explanatory. They are representative of results obtained from the study of a much larger number of somewhat similar aggregates. The salts of lead, copper, iron, and aluminum were found to be the most satisfactory activating agents.

Table 4 gives data for a siliceous bound sandstone. Each particle of aggregate was composed of a large number of small silica grains. The surfaces of such particles of aggregate contain many small cavities, or pockets, between the individual silica grains which are filled with water when wet. In only the shallowest of these pockets did the bitumen completely displace the water.

It can be shown (1) that sharp edges at the entrance to these pockets would greatly hinder the entrance of bitumen even if the inner surfaces of the pockets were wettable by bitumens in the presence of water, particularly so if the bitumen makes a contact angle with the mineral surface.

Adam (2) states that a liquid spreads on the surface of a solid by the evaporation of some of the liquid and its condensation on the solid surface ahead of the spreading liquid. It is, therefore, very probable that one immiscible liquid spreads over a solid surface displacing another immiscible liquid from the surface by a process of solution and condensation. Since the solubility of asphalts in water is low, the replacement of water by bitumen on the inner surfaces of the cavities in the surfaces of particles of sandstone-textured aggregate would be a slow process for medium or coarse gradings of aggregate.

In most paving mixtures however the inner surfaces of such pockets in the surfaces of mineral aggregate particles would be quite well coated due to the presence of a considerable percentage of fines. The coated fines when forced into these pockets during mixing would be expected to coat the insides of the pickets with some of the bitumen carried with them.

Table 1

AGGREGATE-STANDARD OTTAWA SAND

Activator	Acti- vator Ion	Activator Solution cc	Sodium Oleate Solution cc	Remarks
Lead Nitrate	Pb	0.2	0.1	Standard mix
Silver Nitrate	Ag	1.4	0.4	Not as good as standard
Copper Chloride	Cu	0.2	0.1	Like standard
Mercurous Nitrate	Hg	0.6	0.1	" "
Magnesium Chloride	Mg	5.6	8.7	Poor coating
Calcium Chloride	Ca	11.0	15.0	No coating by bitumen
Strontium Nitrate	Sr	8.0	11.5	Poor coating
Barium Chloride	Ba	6.0	8.4	Not as good as standard
Zinc Chloride	Zn	0.8	0.3	Like standard
Cadmium Chloride	Cd	2.5	1.1	Not as good as standard
Mercuric Chloride	Hg	1.1	0.4	" " " " "
Potassium Aluminum Sulphate	Al	0.1	0.1	Like standard
Stannous Chloride	Sn	0.2	nil	" "
Antimony Chloride	Sb	0.05	"	" "
Manganese Chloride	Mn	4.0	2.0	Poor coating
Nickel Chloride	Ni	0.4	0.3	Like standard
Cobalt Chloride	Co	0.6	0.4	" "
Ferric Chloride	Fe	0.3	0.3	" "
Chromium Chloride	Cr	0.3	0.6	" "
Ferrous Ammonium Sulphate	Fe	0.4	0.4	" "

Table 2

AGGREGATE - LIMESTONE

Activator	Acti- vator Ion	Activator Solution cc	Sodium Oleate Solution cc	Remarks
Copper Chloride	Cu	0.6	1.4	Standard mix
Silver Nitrate	Ag	5.2	5.0	Not as good as standard
Mercurous Nitrate	Hg	1.1	2.8	Like standard
Magnesium Chloride	Mg	6.5	14.0	" "
Calcium Chloride	Ca	15.0	17.0	Not as good as standard
Strontium Nitrate	Sr	11.0	20.0	Like standard
Barium Chloride	Ba	4.0	9.0	" "
Zinc Chloride	Zn	0.8	1.4	" "
Cadmium Chloride	Cd	1.0	2.0	" "
Mercuric Chloride	Hg	2.4	5.4	" "
Potassium Aluminum Sulphate	Al	1.0	3.2	" "
Stannous Chloride	Sn	1.4	2.7	" "
Lead Nitrate	Pb	0.8	0.8	" "
Antimony Chloride	Sb	0.2	0.7	" "
Chromium Chloride	Cr	0.6	2.5	" "
Manganese Chloride	Mn	0.7	2.5	" "
Ferric Chloride	Fe	0.8	3.0	" "
Cobalt Chloride	Co	1.2	2.0	" "
Nickel Chloride	Ni	0.6	2.0	" "

Table 3

AGGREGATE - LIGHT COLORED GRANITE

Activator	Acti- vator Ion	Activator Solution cc	Sodium Oleate Solution cc	Remarks
Lead Nitrate	Pb	0.5	0.5	Standard mix
Copper Chloride	Cu	2.0	2.0	Not as good as standard
Mercurous Nitrate	Hg	0.9	0.2	Like standard
Magnesium Chloride	Mg	5.0	7.0	Very poor mix
Barium Chloride	Ba	5.0	4.0	" " "
Zinc Chloride	Zn	4.0	4.0	" " "
Mercuric Chloride	Hg	4.5	3.0	" " "
Potassium Aluminum Sulphate	Al	0.5	1.0	Like standard
Stannous Chloride	Sn	1.5	1.5	" "
Antimony Chloride	Sb	4.0	2.0	Poor mix
Chromium Chloride	Cr	0.7	1.5	Like standard
Manganese Chloride	Mn	2.5	3.0	Very poor mix
Ferric Chloride	Fe	0.5	0.5	Like standard
Cobalt Chloride	Co	3.0	4.5	Poor mix
Nickel Chloride	Ni	2.0	3.0	Not as good as standard

Table 4

AGGREGATE - SILICEOUS BOUND SANDSTONE

Activator	Acti- vator Ion	Activator Solution cc	Sodium Oleate Solution cc	Remarks
Copper Chloride	Cu	2.0	3.0	Standard mix
Lead Nitrate	Pb	2.0	2.0	Like standard
Potassium Aluminum Sulphate	Al	1.0	2.0	Like standard
Chromium Chloride	Cr	2.0	4.0	Not as good as standard
Ferric Chloride	Fe	2.0	3.0	Like standard

Table 5

AGGREGATE - 24 GRAMS OTTAWA SAND
+ 6 GRAMS SILICA DUST PASSING NO. 100

Activator	Acti- vator Ion	Activator Solution cc	Sodium Oleate Solution cc	Remarks
Copper Chloride	Cu	1.4	1.2	Standard mix
Lead Nitrate	Pb	1.7	1.4	Like standard
Potassium Aluminum Sulphate	Al	2.0	2.5	Like standard
Ferric Chloride	Fe	2.5	2.5	" "

Table 5 contains data for an aggregate containing 20 per cent of silica dust as fines. Other tables for varying percentages of silica, limestone, and feldspar dusts, not listed, also indicate that the quantities of reagents required for water replacement are increased by the presence of the fines, although not to a large degree by any means for these particular mixes. Greater quantities of reagents were required for aggregates containing limestone fines than for those containing the same percentage by weight of the silica or feldspar dusts.

Table 6 gives reagent requirements for water displacement on sands from a number of Saskatchewan gravels from widely distributed gravel pits, using lead nitrate as activating agent. The reagent requirements are considerably greater than for the aggregates used for the previous tables. The use of copper chloride as activating agent gave almost identical results.

Table 6

AGGREGATE - GRAVELS FROM DIFFERENT AREAS OF SASKATCHEWAN

Gravel	Lead Nitrate Solution cc	Sodium Oleate Solution cc	Remarks
Radisson	5.0	4.0	Standard mix
Regina	4.0	4.0	Like standard
Rosetown	6.0	3.0	" "
Swift Current #1	3.0	2.0	" "
Swift Current #2	6.0	5.0	" "
Saskatoon #1	3.0	3.0	" "
Saskatoon #2	2.0	2.0	" "
Yorkton #1	4.0	4.0	" "
Yorkton #2	4.0	4.0	" "
Yorkton #3	4.0	4.0	" "
Yorkton #4	9.0	7.0	" "
Yorkton #5	8.0	8.0	" "
Yorkton #6	6.0	6.0	" "
Yorkton #7	6.0	5.0	" "
Yorkton #8	6.0	10.0	" "
North Battleford	1.5	1.5	" "

Table 8 gives the mineralogical analyses of these sands. The granite column includes everything but the limestone and quartz, but the materials were largely granite and feldspar. The mineralogical composition of these sands is fairly uniform.

Table 7

EFFECT OF REMOVING DUST FROM AGGREGATE BY WASHING

Washed Aggregates			
Gravel	Lead Nitrate Solution cc	Sodium Oleate Solution cc	Remarks
Saskatoon #2	0.5	0.7	Standard
Regina	1.5	1.5	Like standard
Yorkton #4	2.0	1.5	" "

Table 8

MINERALOGICAL ANALYSES OF GRAVELS
- 8 + No. 40 Sieve

Gravels	Limestone %	Granite %	Quartz %
Radisson	7.8	53.9	38.3
Regina	20.6	51.5	27.9
Rosetown	20.2	60.6	19.2
Swift Current #1	39.6	52.0	8.4
Swift Current #2	20.5	48.3	31.2
Saskatoon #1	14.3	50.3	35.4
Saskatoon #2	16.0	52.8	31.2
Yorkton #1	29.5	51.5	19.0
Yorkton #2	18.1	62.5	19.4
Yorkton #3	22.3	46.7	31.0
Yorkton #4	24.6	51.2	24.2
Yorkton #5	23.7	45.7	30.6
Yorkton #6	22.7	49.9	27.4
Yorkton #7	19.4	53.4	27.2
Yorkton #8	27.0	53.9	19.1
North Battleford	16.1	66.9	17.0

Due to the fairly uniform mineralogical composition, it was thought that adhering dust might explain the variations observed in table 6, since some of the gravels were very dusty. The sands from three of these gravels were well washed and the reagent requirements for water displacement again determined.

These are listed in table 7. On comparison with the same sands unwashed in table 6, it can be seen that washing has greatly reduced reagent requirements and has also greatly reduced the previous large differences for reagent requirements between these sands.

In table 9 comparisons are made between a number of asphaltic oils, crude oils, and tars as to their natural ability to displace water on the surfaces of particles of wet aggregate. They are compared on the basis of the quantities of reagents required to just give complete water displacement. The activating agent used was lead nitrate. Almost identical results were obtained using copper chloride as activating agent. Considerable variation exists in the abilities of the various bituminous materials to displace water as measured by reagent requirements.

It seemed worth while to examine certain properties of these bitumens in an endeavor to find what factors might be responsible for this variation. It seemed likely that the consistency of the bitumens might be one of these, and possibly their chemical constitution as revealed by the solubility of each bitumen in carbon disulphide, carbon tetrachloride, and paraffin naphtha would be another.

In table 10 the bitumens are listed according to type and locality where procured. The carbene and asphaltene content of each bitumen is given together with its viscosity. In some cases samples of the crude from which a road oil was made were available. A crude is designated by the number of the asphalt made from it, followed by the letter c.

While the data given in tables 9 and 10, and other data obtained by the writer, are somewhat meagre for the purpose of making generalizations to explain the variations in the natural ability of bituminous materials (in terms of reagent requirements) to displace water on wet mineral aggregates, a study of the data available leads to two generalizations which are at least reasonable.

- (1) For bituminous materials from the same source and of equal asphaltene plus carbene content, that bitumen having the highest viscosity has the greatest ability to displace water on the surfaces of the particles of a wet mineral aggregate.
- (2) 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 term "the same source" in these two generalizations means that the bituminous materials have resulted from the same crude or feed and the same process of manufacture.

Best illustrations of the first generalization are bitumens 9 and 10, and 6 and 6c. It has also been observed that for bitumens from the same source, S. C. 4 or M. C. 4 has

Table 9

WATER DISPLACEMENT WITH VARIOUS BITUMENS

Aggregate - Saskatoon Gravel #2

Bitu- men No.	Type	Source	Lead Nitrate Solution	Sodium Oleate Solution	Remarks
1	Road Oil	Saskatchewan	2.0	2.0	Standard mix
2	Cut-back	"	1.5	1.0	Like standard
3	Road Oil	Arkansas	2.0	2.0	" "
3c	Crude for 3	"	5.0	4.0	" "
4	Road Oil	California	2.0	1.5	" "
4c	Crude for 4	"	2.5	2.5	" "
5	Road Oil	Wyoming	1.5	1.0	" "
6	" "	" "	2.0	2.0	" "
6c	Crude for 6	"	4.0	4.0	" "
7	Road Oil	Illinois	1.5	1.5	" "
8	" "	Kansas	1.5	1.5	" "
9	" "	California	1.5	1.5	" "
10	" "	"	2.0	2.0	" "
11	Light Tar	New York	1.5	1.0	" "
12	Heavy Tar	" "	1.5	1.5	" "

Table 10

ANALYSIS OF BITUMINOUS MATERIALS

Bitu- men No.	Soluble in Carbon Di- sulphide (Total Bitumen)	Bitumen in- soluble in Carbon Tet- rachloride (Carbenes)	Bitumen soluble in Carbon Tetrachloride Insoluble in Paraffin Naphtha (Asphaltenes)	Viscosity in Saybolt Furol at 122° F. Sec.
	%	%	%	
1	99.82	3.6	7.4	187
2	99.90	2.40	14.7	217
3	99.64	0.0	7.8	270
3c	99.85	0.07	3.3	29
4	99.94	0.04	12.1	381
4c	99.91	0.0	10.4	290
5	99.87	1.15	9.1	296
6	99.91	0.0	6.5	348
6c	99.93	0.0	8.7	29
7	99.76	1.53	8.4	151
8	99.91	0.96	12.0	356
9	99.93	0.0	1.7	353
10	99.96	0.0	1.1	145
11	96.32	4.9	11.2	33
12	91.30	8.0	14.0	101

greater ability to replace water than S. C. 2 or M. C. 2, respectively, although the asphaltene and carbene contents are approximately the same.

Examples illustrating the second generalization are bitumens 1 and 2, 5 and 6, 4 and 4c. It has been observed further that for bitumens of the same viscosity and from the same source, R. C. bitumens have greater water displacing ability than M.C. bitumens, and these in turn than S. C. bitumens. For bitumens from the same source, and of the same viscosity, in general, R. C. bitumens have a greater asphaltene plus carbene content than M. C. bitumens, and these in turn have a greater asphaltene plus carbene content than S. C. bitumens.

The following purely mechanical reason is offered as a possible explanation for the first generalization. The hydrocarbon film formed by the reaction of activating and wetting agents on the surface of a mineral particle consists of a great number of points where the water-repelling, bitumen-attracting, hydrocarbon chains of the attached fatty acid radicals are oriented outwards from the mineral surface (Fig. 19). The greater the quantities of reagents used the greater is the density of such points on the surface of each aggregate particle up to the closest possible packing of the chains. Between these water-repelling points the mineral surface is still water attractive except when the monomolecular film is complete.

For a bituminous oil of low viscosity, it would be expected that these bitumen-attracting points must be much closer together for the film of bitumen to withstand a given stress set up by particles of aggregate rubbing against each other during mixing than would be necessary for a bituminous oil of much higher viscosity, other factors being the same, since viscosity is a measure of the strength of the film. Consequently a greater quantity of reagents would be required when water displacement is being effected by the lower viscosity bitumen.

It is more difficult to determine a reasonable explanation for the second generalization, but the following is suggested. Mineral aggregates used for bituminous surfacings in general are polar materials. The asphaltenes and carbenes are the most polar constituents of a petroleum asphalt, the resins and oily constituents being the least polar. Considerable attraction exists naturally between the polar asphaltenes and carbenes and a mineral surface due to the thermodynamic tendency of each to decrease the free energy in the electric fields surrounding their dipoles, but the higher adhesion tension between the mineral surface and water prevents the bitumen from gaining a foothold on a wet mineral surface unaided. However, with the assistance of a few bitumen-attractive, water-repelling points on the wet

mineral surface furnished by the hydrocarbon chains of the activating agent wetting agent combination, at which the oily portions of the bitumen can establish contact, complete water displacement follows if the surface density of such points is sufficiently great. The density of such bitumen-attracting points (the quantity of reagents) required for any bitumen to displace water on a mineral surface, depends on the natural attraction of the bitumen for the mineral surface. Since this natural attraction seems to depend a great deal on the asphaltene plus carbene content of a bitumen, this explanation appears reasonable.

It should be observed, however, that bitumens 1 and 10 have the same natural ability to displace water (as measured by reagent requirements) in spite of the fact that bitumen 1 has ten times the asphaltene plus carbene content of bitumen 10. Thus the chemical composition of the asphaltenes and carbenes, or the degree of dispersion or flocculation of these in any bitumen, or both, also has a large effect.

It is possible and rather likely that other factors not disclosed by the data in table 10 also play a part.

There is the possibility, by the use of wetting and activating agents for the coating of wet aggregates with bituminous materials, of quantitatively comparing the natural affinity of each of a number of bituminous materials for a given aggregate. The bitumen which coated the thoroughly wetted aggregate through the use of the smallest quantities of wetting and activating agents, would, on the basis of the discussion presented immediately above, have the greatest natural affinity for the aggregate. This method, however, would have to be further investigated before being considered as a standard test of the affinity of a bitumen for an aggregate.

From table 11 it may be observed that the quantity of water present with the aggregate has almost no effect on the quantities of reagents required to effect displacement of the water by a bitumen. This is no doubt due to the very low solubility of the compounds resulting from the reaction of the wetting and activating agents at the mineral surfaces. The quantity of water present, however, must not be sufficiently great to float the bitumen beyond the reach of the aggregate during mixing. The water content should be held below the point where the mixture takes on the properties of a suspension, so as to develop some resistance to shear, upon which rapid coating action seems to largely depend even when the aggregate is dry.

Table 12 shows that reagent requirements are reduced by increasing the bitumen content of a mix. This would be expected on the basis of the greater mechanical strength of the thicker film of bitumen, following the explanation offered for the first generalization in the discussion of table 10.

Table 11

EFFECT OF INCREASING THE WATER CONTENT IN A MIXTURE

Aggregate - Saskatoon Gravel #2			
Amount of Water Added to Mix	Lead Nitrate Solution cc	Sodium Oleate Solution cc	Remarks
2 grams	1.4	1.2	Standard mix
5 "	1.2	1.0	Like standard
10 "	1.3	1.2	" "
20 "	1.4	1.2	" "

Table 12

EFFECT OF INCREASING BITUMEN CONTENT IN A MIXTURE

Aggregate - Radisson Gravel					
Activator	Weight of Bitumen Used	Acti- vator Ion	Activator Solution cc	Sodium Oleate Solution cc	Remarks
Copper Chloride	1 gram	Cu	3.0	2.5	Standard Mix
Lead Nitrate	1 "	Pb	5.0	4.0	Like standard
Copper Chloride	2 "	Cu	2.5	1.5	" "
Lead Nitrate	2 "	Pb	3.0	3.0	" "

In the course of this investigation it was observed that when the proper quantities of reagents were present, the mixing time was possibly less than that required for dry mixes, at least on a laboratory scale.

The required reagents are equally effective if added as water solutions, or dissolved or suspended in the bituminous material, or used in a bituminous emulsion, or added in any combination of these.

While sodium oleate was the most commonly used wetting agent during this research, tests indicated that a great many other organic compounds give highly satisfactory results. A few of these other wetting agents found satisfactory are

sodium stearate, oleic acid, linseed soap, cheap washing soaps, and the potassium salts of asphaltic acids obtained by water-washing after refluxing a benzene solution of natural asphalt with alcoholic potash.

The Proportioning of Wetting and Activating Agents

There is little in flotation literature to lead one to believe that the way in which the wetting and activating agents might be proportioned in any mixture, would have any effect on the displacement of water by bitumen on the surfaces of the particles of a wet mineral aggregate. The quantitative references to this which the writer has found are somewhat confusing, and in some cases at least (3), indicate that an excess of activating agent inhibits flotation.

However, it was observed early in this investigation that an excess of soap prevented the coating of wet siliceous aggregates by bitumens, and also caused stripping of coatings already formed. An investigation was made, therefore, to determine if possible, just how wetting and activating agents should be proportioned in order that water displacement by bitumens on wet aggregates could be accomplished by a minimum of these reagents.

The experimental procedure consisted of adding a measured quantity of activating agent solution to a water-aggregate-bitumen mixture, and by adding small quantities of wetting agent solution, determining the quantity of wetting agent solution which gave the best coating, and the amount which caused complete or almost complete stripping. This was repeated for various quantities of activating agent.

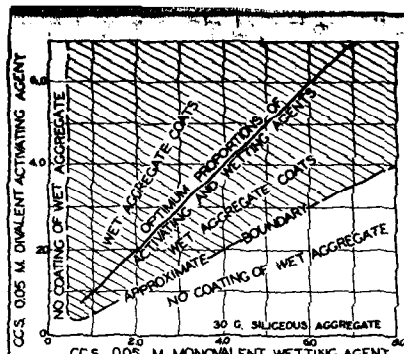
The results obtained were checked by starting with a measured quantity of soap solution (wetting agent) and adding measured amounts of activating agent.

The aggregates used were a red granite, Ottawa sand, and sand from a natural gravel.

Tables are not very satisfactory for tabulating the observations recorded, but the experimental results are listed graphically in Figs. 4 and 6.

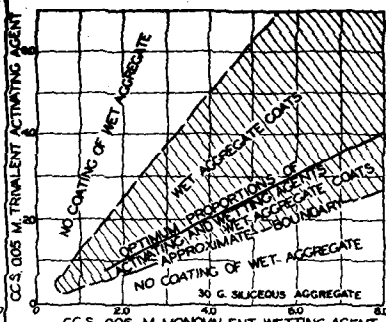
From Fig. 4 it appears that when the activating agent is divalent, optimum reagent proportions are about one equivalent of wetting agent to each two equivalents of activating agent. Coating of wet aggregates by bitumen was either impossible or unsatisfactory if the wetting and activating agent were present in the proportions of one or more equivalents of wetting agent per equivalent of activating agent.

From Fig. 6 it appears that when the activating agent is trivalent, optimum reagent proportions are about two equivalents of wetting agent to three equivalents of activating agent, and coating was either impossible or unsatisfactory if the reagents were reacted in the proportions of one or more equivalents of wetting agent per equivalent of activating agent.



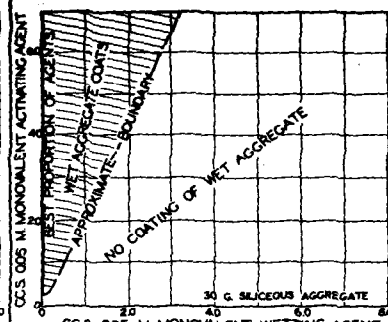
CC.S. 0.05 M. MONOVALENT WETTING AGENT
MONOVALENT WETTING AGENT
DIVALENT ACTIVATING AGENT CURVES

FIGURE 4



CC.S. 0.05 M. MONOVALENT WETTING AGENT
MONOVALENT WETTING AGENT
TRIVALENT ACTIVATING AGENT CURVES

FIGURE 6



CC.S. 0.05 M. MONOVALENT WETTING AGENT
MONOVALENT WETTING AGENT
MONOVALENT ACTIVATING AGENT CURVES

FIGURE 8

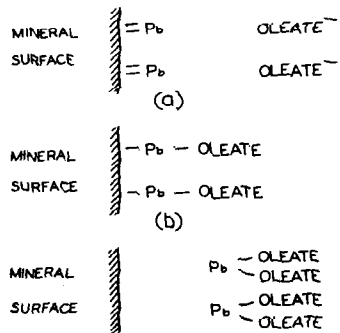


FIGURE 5

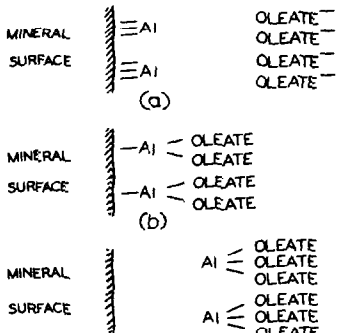


FIGURE 7

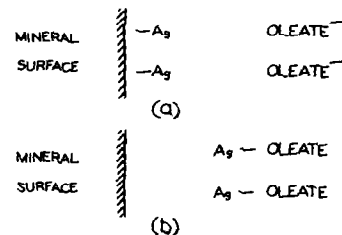


FIGURE 9

A possible reason for these experimental observations becomes apparent from a study of the ionic and molecular diagrams of Figs. 5 and 7.

Figs. 5a and 7a represent the condition of a siliceous aggregate surface, presumably as the result of a base exchange, after the activating agent has been added, but before there has been any reaction with the oleate radicles.

Figs. 5b and 7b represent the same surfaces respectively, after the activator ions have reacted with the oleate radicles. The resulting compound is held to the mineral surface by a lone primary valence in each case. The hydrocarbon ends of the oleate radicles make the surface water-repellent and bitumen attractive at such points. The proportions of reagents for this condition of the mineral surface are represented by the experimentally determined heavy line labeled "optimum proportions" in each of Figs. 4 and 6 respectively.

It should be pointed out that in Figs. 5b and 7b the valences between the activator ion and mineral surface are electrovalences which render these compounds insoluble in organic liquids, while the valences between the activating ions and wetting agent radicals are covalences which make the compounds insoluble in water. Consequently, compounds of this type are insoluble in both water and bituminous materials.

Figs. 5c and 7c show that when the wetting and activating agents are reacted in stoichiometrical equivalents, the mineral surface loses the water-repellency and bitumen-attractiveness it possessed in Figs. 5b and 7b because sufficient wetting agent has been added to saturate the primary valences of all the activator ions present on the mineral surface. There is no primary valence left to hold the molecules of the resulting compounds to the mineral surface, and these are dissolved off the surface by the bituminous material present in which they are soluble. The experimentally determined right-hand branch of the broken line curve labeled "approximate boundary" in Figs. 4 and 6 also represents stoichiometric proportions of activating and wetting agents.

While the data obtained for Fig. 4 give the actual position of the left-hand branch of the broken line curve labeled "approximate boundary" with reasonable accuracy, there has not so far been occasion to determine the exact position of this branch of this curve in Fig. 6 with the same accuracy, consequently its position in this latter figure must be considered tentative only, for the present.

That no water displacement occurred, or only very poorly, when the reagents were reacted at the surfaces of siliceous aggregates in the proportions of one or more equivalents of wetting agent to each equivalent of activating agent, was further proven by the following:

In all cases, the salts of calcium, strontium, barium, and magnesium were very unsatisfactory or useless as activating agents for siliceous aggregates.

From a study of Fig. 5b, it would appear on thermodynamic grounds that more free energy is released by the union of a wetting agent radical with the first valence of a lead ion adsorbed by a siliceous mineral surface than with the second. Consequently, wetting agent radicals tend at first to attack only one valence of each adsorbed lead ion, leaving the other valence attached to the mineral surface. Wetting agent radicals in excess of the quantity required for this, attack the remaining valence giving the condition in Fig. 5c in which no primary valence remains to attach the resulting lead oleate to the mineral surface.

The lack of appreciable ability on the part of salts of the alkali earth metals and magnesium to function as activating agents in the presence of bituminous materials, would be explained, if approximately as much free energy was released by the union of a wetting agent radical with the second as with the first valence of an adsorbed ion of these metals. If this were so, wetting agent radicals would tend to react with both valences of an adsorbed calcium ion (Fig. 10c) as readily as with only one valence of each of a number of adsorbed calcium ions (Fig. 10b). However, it would be unusual and unlikely for these two free energies to be exactly the same.

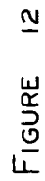
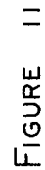
In Fig. 10, it should be emphasized that Fig. 10c appears to represent what occurs when calcium is used as an activating agent when bituminous materials are present, and not Fig. 10b.

Materials like calcium oleate are quite soluble in bituminous materials. Consequently, even if calcium has normally some ability to function as an activating agent, as shown in Fig. 10b, the tendency of the bitumen present to dissolve calcium oleate from a mineral surface would tend to cause the reaction shown in Figs. 10b to c to occur, just as concentrated sulphuric acid can extract water from organic compounds in which water is not present as such. The reaction shown in Figs. 10b to c would be thermodynamically possible if the energy of solution of calcium oleate in the bitumen were greater than the difference in the free energies released by the union of each valence of an adsorbed calcium ion with an oleate radical.

The writer does not deny the possibility that compounds of the type shown in Figs. 5c, 7c, and 10c may be adsorbed on the surfaces of mineral aggregates by means of secondary valence forces. However, for the coating of wet siliceous aggregates with bituminous materials, such compounds appear to play at most only a very minor rôle, the major rôle being played by compounds which are capable of being adsorbed by means of primary valence.



FIGURE 10



It is interesting in this connection that it was found that the basic dye, methylene blue, was able to bring about the coating of wet siliceous materials by bitumens. The water-repellent hydrocarbon group is in the cation of this compound, whereas it is in the anion of soaps and related materials. Consequently, the methylene blue radical as a result of the base exchange reaction, shown in Fig. 11, is capable of conferring water-repelling, bitumen-attracting properties on a silicate particle without the necessity for an activating agent. It is generally conceded by those who have studied the interaction of methylene blue with siliceous materials that a strict exchange adsorption takes place between the methylene blue cations and metallic cations of the silicate. Consequently, only primary valence forces are involved in this adsorption.

This action of methylene blue indicates that basic organic compounds of the amine, pyridine, quinoline, etc., types, or derivatives of these, some of which are found in bituminous materials themselves, might be developed as successful wetting agents for the coating of wet aggregates with bituminous materials, or for increasing the adhesion tension between aggregates and bitumens. The advantage in the use of such reagents lies in the fact that an activating agent of the type so far considered would not be necessary, and a saving in reagent requirements might be thereby effected. However, the quantity of methylene blue required for water displacement on aggregates so far studied has always been very much greater than the amount of soap or similar wetting agent, and activating agent, required. It is possible that the use of activating agents containing a polyvalent anion such as sodium silicate, trisodium phosphate, etc., would be desirable when using these basic organic compounds as wetting agents.

It should be emphasized that the experimental results and theoretical discussion up to this point have pertained to siliceous aggregates only.

Only a small amount of work has been so far done with limestone aggregates. This has shown that limestone aggregates may be as readily coated while wet through the use of the proper reagents as siliceous materials.

Results to date, however, tend to indicate that compounds of the type shown in Fig. 12 are of most importance in bringing about the coating of wet limestone. Compare the results in table 2 with those in other tables where siliceous aggregates were used. There has been no evidence up to the present time that compounds like those in Figs. 5b and 7b joined to the limestone surface by primary valence are formed, although the amount of investigation carried out so far does not warrant the expression of more than a tentative conclusion.

The following are a few observations which tend to substantiate this very tentative conclusion:

Methylene blue is of no value whatsoever for bringing about the coating of any wet limestone so far studied.

For those limestones which will not coat with bitumens while wet with the use of soap alone, aluminum ion functions as a satisfactory activating agent, and in some cases silver ion also. It appears that aluminum carbonate cannot exist in water, being hydrolyzed to aluminum hydroxide and carbonic acid. It is unlikely, therefore, that aluminum ion, or any compound of aluminum ion with a wetting agent (Fig. 7b) could be attached to a limestone surface by primary valence, for any such valence would tend to be broken immediately by hydrolysis in the presence of water. It has been previously pointed out that when the lone primary valence on a silver ion is attached to a wetting agent radical, there is no primary valence left for attaching the resulting compound to a mineral surface.

The metallic soaps, like those shown in Fig. 12, may bring about water displacement by bitumens on wet limestone surfaces either by being held to the limestone by strong secondary valence forces, as emulsifying agents, or both.

CONCLUSIONS

The writer wishes to emphasize that the theoretical conclusions presented below, or in any section of Part I of this paper, have been derived from a study of the water-aggregate-bitumen system. The conclusions presented will not necessarily apply to any other system.

A. Theoretical

1. By the application of some of the general principles of ore flotation theory, it has been shown how wet mineral aggregates may be coated with bituminous materials.

2. It was found to be quite possible to displace the water with bitumen on each of the aggregates investigated after these had been thoroughly wetted with water, through the use of activating and wetting agents.

3. Activating agents have been required in addition to wetting agents for all siliceous aggregates so far studied, but are not required for all limestone aggregates.

4. The most effective activating agents appear to be the salts of lead, copper, aluminum, and iron.

5. The quantity of water present had no noticeable effect on reagent requirements.

6. Increasing the percentage of bitumen reduced the reagent requirements.

7. Aggregates whose particles possessed a sandstone texture were most difficult to coat completely.

8. The reagent requirements for effecting water displacement by bitumen on any one aggregate varied appreciably for different bitumens.

9. For bitumens from the same source, reagent requirements for water displacement, in general decrease as the viscosity, and asphaltene and carbene contents, increase.

10. When the proper quantities of reagents are present, the mixing time is possibly less than that required for dry mixes, at least on a laboratory scale.

11. The required reagents are equally effective if added as water solutions, or dissolved or suspended in a bituminous material, or used in a bituminous emulsion, or added in any combination of these.

12. Compounds formed at the surfaces of wet siliceous aggregates by the reaction of wetting and activating agents must be attached to the mineral surface by primary valence in order to bring about displacement of the water by bituminous materials.

This conception affords a reasonable explanation of the ability of most multivalent metallic cations to function as activating agents, and of the inability of monovalent metal cations like silver, and of the divalent alkali earth metal cations and magnesium, to function in an activating capacity, where siliceous minerals are concerned.

The ability of methylene blue, a basic dye, to bring about the coating of wet siliceous aggregates with bituminous materials is also rationally explained by this conception.

13. Stoichiometrical equivalents of activating and wetting agents appear to be the optimum proportions of these reagents for bringing about water displacement by bitumens on the surfaces of wet limestone aggregates.

14. It appears to be possible to quantitatively compare the natural affinity of various bitumens for any mineral aggregate, by determining the amount of wetting and activating agents required to bring about the displacement of water on the particles of the thoroughly wetted aggregate with each of the various bitumens.

B. Practical

1. In the absence of actual field tests no definite conclusions can be safely drawn as to the practical possibilities of the method outlined here for producing bituminous mixtures for various engineering purposes. On the basis of laboratory tests, the aggregates used for bituminous surfaces could be coated with bitumen while wet at a reagent cost for many aggregates at least, of from five to fifty cents per ton of aggregate treated.

The initial reaction of many engineers to this will be that it would be as cheap or cheaper on projects of any size to dry the aggregate.

2. It should be pointed out, however, that in bituminous mixtures coated while wet through the use of these reagents, the adhesion tension of the aggregate has been made permanently greater for bituminous materials than for water. This might lead to worth while savings in maintenance costs.

3. The method should be valuable in those locations where water action is severe, or for aggregates from which bitumen is easily stripped by water.

4. Since no drying is required, this method is of particular value wherever the use of cold laid materials is possible. Through the use of cut-backs, or of flux oils and powdered asphalts, bituminous mixtures containing bitumens of any desired final consistency could be laid cold.

5. Finally, it must be recognized that the reagent cost even on a laboratory scale places this method at least very close to competing in cost with drying the aggregate. In ore flotation processes it has been found that reagent requirements on a plant-size scale are generally much lower than on a laboratory scale.

Research might disclose more efficient reagents than those which the writer has so far used.

Even a moderate reduction in reagent requirements due to the greater efficiency of plant-scale operation, or to more efficient reagents, would make it cheaper to coat many mineral aggregates by this process than through the use of the drier.

PART II

THE STABILIZATION OF SOILS

Part II of this paper presents the results of some fundamental research on the physical chemistry of soil stabilization which has been carried out by the writer during the tenure of a University of Michigan Fellowship in 1936, and of Department of Engineering Research Fellowships in 1936-37, and in 1937-38, at the University of Michigan, sponsored by the Michigan State Highway Department. The writer wishes to gratefully acknowledge the assistance afforded by these fellowships in carrying out this research. The progressive attitude shown by the Michigan State Highway Department in sponsoring fundamental research in this manner cannot be too highly commended, and the writer wishes to express appreciation for the interest shown by State Highway Commissioner Murray D. Van Wagoner, Research and Testing Engineer W. W. McLaughlin, and Mr. McLaughlin's predecessor, J. W. Kushing.

The writer also wishes to express his sincere appreciation to Professor W. J. Emmons and Professor W. S. Housel, of the Department of Civil Engineering at the University of Michigan, for their encouragement and their interest in this research.

Introduction

Most highway engineers would no doubt agree that the millenium in highway construction had been reached, if it were possible to use any available local material, including silts and clays, for subgrade construction, to lay the required surfacing on this, and know that differential heaving and settling of the road surface due to frost heave, frost boils, or fluctuating moisture content, could not occur.

In attempting to remedy the deleterious effect of water on subgrades, highway engineers have used various drainage measures, excavation of undesirable soil materials, Proctor technique, and several methods of soil stabilization.

There are conditions under which none of these methods are satisfactory for subgrade construction, and not one of these methods, with the possible exception of the stabilization of certain soils with certain bituminous materials, is capable of eliminating the effects of water on the subgrade under all conditions, nor is it possible to make use of all soil materials in any locality as they are encountered in the soil profile during construction by any of these methods.

It is the purpose of Part II of this paper to show how the entrance of water into soils may be inhibited, and even entirely prevented, by making them capillary repulsive to water.

Incidentally, the data which will be presented tend to show that the use of soaps by themselves in the oiling of earth roads is likely to be of very little, if any, value.

Theory

The well known equation for the height of rise of a liquid in a fine capillary tube is

$$h = \frac{2S \cos \theta}{g r d} \quad (2)$$

where h = height of rise of a liquid in the capillary tube above the free surface of the liquid;
 S = surface tension of the liquid;
 g = acceleration due to gravity;
 r = radius of capillary tube;
 d = density of the liquid;
 θ = contact angle made by the liquid with the walls of the capillary tube.

While soil materials do not necessarily behave like a bundle of capillary tubes, the conclusions drawn in this paper are qualitatively the same regardless of the theory used to explain the rise of water in soils by capillary activity.

From the very nature of the factors S, g, r, and d on the right-hand side of Eq. (2), it is obvious that the small amount of change possible in these, would at best have only an inappreciable effect on h for any one soil.

The average radius r of the soil pores is a constant for any soil in given condition, and can only be changed appreciably by admixtures of other soil materials.

The density d of the water in a soil depends on the temperature of the soil, and on the concentration of dissolved salts, but is only negligibly affected by these for the purposes of this problem.

The gravitational constant g changes slightly with latitude and altitude, but these changes are negligible as far as this problem is concerned.

While the surface tension S of water in soil could be changed appreciably by certain surface active substances, the reduction at best would be to approximately one half of the value for pure water, and these substances which are often quite soluble, would soon be so widely dispersed, or so completely removed by reaction with the soil materials, that the surface tension would quickly revert to approximately its original value.

The possible effect on h of a change in θ , the angle of contact made by water against the soil particles, however, can be very marked. A capillary attraction can be changed

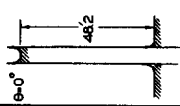
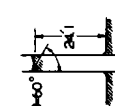

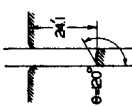
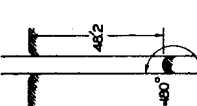
<p> $h = \frac{2S \cos \theta}{\rho r d}$ </p> <p> h = HEIGHT OF CAPILLARY RISE. S = SURFACE TENSION 72 DYNES/CM IN WATER ρ = GRAVITATIONAL CONSTANT 981 CM/SEC. d = DENSITY OF LIQUID WATER = 1.00 r = AVERAGE RADIUS OF CAPILLARY SOIL PORE. θ = CONTACT ANGLE. IN FIGURES 14 THROUGH 18, $r = 0.001$ CM. </p>	<p> CASE 1 $\theta = 0^\circ$ $\cos \theta = 1$ $h = \frac{(2)(72)(1)}{(981)(0.001)}$ = 1470 CM. = 482 FT. </p> 	<p> CASE 2 $\theta = 60^\circ$ $\cos \theta = \frac{1}{2}$ $h = \frac{(2)(72)(0.5)}{(981)(0.001)}$ = 735 CM. = 24.1 FT. </p> 
<p> CASE 3 $\theta = 90^\circ$ $\cos \theta = 0$ $h = \frac{(2)(72)(0)}{(981)(0.001)}$ = 0.0 CM. = 0.0 FT. </p> 	<p> CASE 4 $\theta = 120^\circ$ $\cos \theta = -\frac{1}{2}$ $h = \frac{(2)(72)(-0.5)}{(981)(0.001)}$ = -735 CM. = -24.1 FT. </p> 	<p> CASE 5 $\theta = 180^\circ$ $\cos \theta = -1$ $h = \frac{(2)(72)(-1)}{(981)(0.001)}$ = -1470 CM. = -482 FT. </p> 

FIGURE 15

FIGURE 14

FIGURE 13

FIGURE 18

FIGURE 17

FIGURE 16

to a capillary repulsion by suitably controlling this contact angle. This can best be illustrated by considering a number of cases where various values are substituted for θ in Eq. (2).

First however, the term "contact angle" should possibly be defined. It is the angle, measured through the liquid phase, between the surface of the solid and the tangent to the curve of the surface of the liquid at the point of contact of the liquid on the solid, air being the third phase (Figs. 14 to 18).

Consider a clay soil of particle size 0.002 cm diameter,

Then $r = 0.0001$ cm approximately.

Also $g = 981$ cm/sec.²,

and $S = 72$ dynes/cm for water.

Fig. 14 shows that when $\theta = 0^\circ$, the usual value of the contact angle of water against soil, the height of capillary rise in this soil is theoretically 48.2 feet above a free water level. With such a soil, if 3 feet of subgrade were to be kept free from water, drains would have to be installed 52.2 feet below the surface of the subgrade in order to keep the free water level at this depth.

For the case where $\theta = 60^\circ$, Fig. 15 shows that if 3 feet of subgrade are to be kept free from capillary water, drains would have to be installed 24.1 feet below the surface of the subgrade.

When $\theta = 90^\circ$ (Fig. 16), there is no capillary rise, and drains placed 3 feet below the surface of the subgrade would insure that a 3-foot depth of subgrade was free from capillary water.

When $\theta = 120^\circ$ (Fig. 17), a 3-foot embankment would be free from capillary water as long as the free water level was not more than 21.1 feet above the level of the surface of the embankment.

When $\theta = 180^\circ$ (Fig. 18), (incidentally, a case not possible of even theoretical attainment as an equilibrium value with real materials), there would be no capillary water in a 3-foot subgrade as long as the free water level was not more than 45.2 feet above the level of the surface of the embankment.

It is, therefore, obvious that the height of rise of water in a soil subgrade could be controlled, and the soil even rendered capillary repulsive to water, if it were possible to control the contact angle between soil and water.

Many engineers have no doubt observed that water does not rise as high in a greasy as in a clean glass capillary tube of the same diameter. This is due to the fact that water makes a contact angle against a greasy surface, and none against clean glass.

In spite of this observation it does not appear to be generally known that a contact angle between water and almost any solid surface can be developed by the use of the proper chemical reagents, even though originally there was no angle of contact. It will shortly be demonstrated that soils are no exception to this.

In the ore flotation processes previously mentioned, by the addition of certain chemical reagents, the surfaces of valuable mineral particles are made to develop a contact angle against water. This brings about their attachment to the air bubbles present, and causes their separation from the useless gangue minerals which do not develop a contact angle by the use of the same reagents.

This contact angle is developed because the reagents used make the surfaces of the particles water-repellent, and make them behave as though each were coated with a greasy film.

The size of the contact angle depends on both the kind and concentration of the reagents used. Using xanthates, Wark and Cox (5) have shown that contact angles varying from 50° to 96° can be developed on the surfaces of mineral sulphides, as the hydrocarbon chain in the xanthate is increased from one to sixteen carbon atoms in length. The same workers showed that xanthates containing simple aromatic and naphthene groupings develop contact angles which vary only from 71° to 75° . Siedler (6) has shown that sodium oleate, the chief ingredient of many toilet soaps, will develop a contact angle of 102° against calcite, and that sodium stearate will develop a contact angle of 121° against the same mineral.

It appeared possible at the beginning of this investigation therefore, that by the use of certain chemical reagents, the capillary attraction between soil and water could not only be greatly reduced, but even changed to a capillary repulsion, since any contact angle greater than 90° would bring about such a repulsion.

The same general flotation theory which was applied in Part I to the problem of coating wet mineral aggregates with bituminous materials, can be applied to the problem of making soils capillary repulsive to water, through the use of the same activating and wetting agents whose functions have already been demonstrated.

Fig. 19 gives a molecular picture of the surface of a siliceous particle which has been made water-repellent at one point by the use of a lead salt as activating agent, and sodium stearate as wetting agent.

It should be obvious that the water-repellency of a mineral surface depends on the surface density of such water-repellent points, and on the length or structure of the hydrocarbon groups, and therefore, on the concentration and types of reagents.

Since the magnitude of the contact angle depends on the water repellency, it follows that the size of the contact angle depends on these same two factors.

It is apparent, therefore, that the magnitude of the contact angle in this case, is a measure of the statistical average of the water-repellency due to the hydrocarbon groups and of the water-attractiveness of the mineral surface between these hydrocarbon groups.

A Method for Measuring the Contact Angles Developed in Mineral Powders

Ordinary soil materials show zero contact angle against water. Since it was proposed to develop a contact angle of varying magnitude between soil particles and water through the use of certain chemical reagents, it was necessary to have a simple and convenient method for measuring the size of contact angle developed.

Without going further into the reasons for the method selected, the method of sedimentation volumes, which has already been used by Bartell and Walton (7), and by Mack (8), for somewhat different purposes, was adopted.

These investigators have shown that a linear relationship exists, if the sedimentation volumes of a given weight of a powder in each of a series of organic liquids are plotted versus the interfacial tensions of these liquids against water (Figs. 21, 22, and 23).

In the work which the writer was undertaking, the differences in the contact angles between the various treated powders and water would be shown by differences in the slope of these straight lines if each of these powders contained particles of the same size distribution, shape, and specific gravity.

Experimental Procedure

The data reported here were all obtained using one wetting agent, sodium oleate, and a number of activating agents, as chemical reagents, and silica dust, limestone dust, and a natural silt, as mineral powders.

The effectiveness of the various activating agents was studied by working with a pure silica powder, since pure silica particles in pure water have no cations at their surfaces which can function as activating agents.

The various chemical treatments given to each mineral powder are listed in tables 13, 15, and 17.

Except where stated to be otherwise (see footnotes after tables 13 and 15), the method of treatment was as follows:

100 grams of the powder were placed in a 600 cc beaker. The indicated amount of activating agent solution was added. Enough distilled water was added

Table 13
CHEMICAL TREATMENTS OF SILICA POWDER

100-gram lots of silica powder passing No. 150 sieve							
Reagents	1	2	3	Powder Number			
	Control			4*	5	6*	7
Activating Agent	Nil	Nil	Calcium Chloride	Calcium Chloride	Lead Nitrate	Lead Nitrate	Potassium Aluminum Sulphate
0.05M Activating Agent Solution, cc	Nil	Nil	60	60	60	60	60
0.05M Sodium Oleate Solution, cc	Nil	60	60	120	60	120	120

*Calcium oleate and lead oleate equivalent to the reagent quantities shown for powders 4 and 6 respectively, were dissolved in carbon tetrachloride and added to respective lots of dry silica dust in this form.

Table 14

SEDIMENTATION VOLUMES OF THE TREATED SILICA POWDERS

10 grams of powder		Powder Number						
Organic Liquids	Interfacial Tension Against Water dynes/cm	1	2	3	4	5	6	7
		cc	cc	cc	cc	cc	cc	cc
Carbon Disulphide	48.1	14.10	12.85	13.20	11.70	9.20	12.87	9.50
Benzene	34.6	12.05	11.40	11.50	11.10	8.50	11.31	9.25
Chloroform	31.6	11.40	10.85	10.81	10.35	8.73	10.88	9.33
n-butyl Acetate	13.2	8.40	8.70	8.52	7.85	8.32	8.58	9.28

Table 15

CHEMICAL TREATMENTS OF LIMESTONE POWDER

100-gram lots of limestone dust passing No. 150 sieve					
Reagents	Powder Number				
	8	9	10	11*	12*
	Control				
Activating Agent	Nil	Nil	Lead Nitrate	Lead Nitrate	Calcium Chloride
0.05M Activating Agent Solution, cc	Nil	Nil	60	60	60
0.05M Sodium Oleate Solution, cc	Nil	60	60	120	120

*Lead oleate and calcium oleate equivalent to the reagent quantities shown for powders 11 and 12 respectively, were dissolved in carbon tetrachloride and added to respective lots of dry limestone dust in this form.

Table 16

SEDIMENTATION VOLUMES OF THE TREATED LIMESTONE DUST

10 grams of powder						
Organic Liquids	Interfacial Tension Against Water dynes/cm	Powder Number				
		8	9	10	11	12
Carbon Disulphide	48.1	11.07	6.62	7.15	6.70	6.43
Benzene	34.6	10.00	6.63	7.16	6.59	6.58
Chloroform	31.6	9.75	6.60	7.10	6.66	6.35
n-butyl Acetate	13.2	7.75	6.95	7.46	7.00	6.90

Table 17

CHEMICAL TREATMENTS OF TUSCOLA SILT

100-gram lots of Tuscola silt passing No. 150 sieve				
Reagents	Powder Number			
	13	14	15	
	Control			
Activating Agent	Nil	Nil	Lead Nitrate	
0.05M Activating Agent Solution, cc	Nil	Nil	60	
0.05M Sodium Oleate Solution, cc	Nil	60	60	

Table 18

SEDIMENTATION VOLUMES OF THE TREATED TUSCOLA SILT

10 grams of powder				
Organic Liquids	Interfacial Tension Against Water dynes/cm	Powder Number		
		13	14	15
Carbon Disulphide	48.1	12.20	10.43	9.27
Benzene	34.6	11.20	9.90	9.11
Chloroform	31.6	11.07	9.75	9.33
n-butyl Acetate	13.2	9.43	9.00	9.00

to make 100 cc. of solution, which was sufficient to form a suspension of the powder upon stirring. After standing for a day with occasional stirring, the amount of wetting agent listed was added. This mixture was allowed to stand for another day with occasional stirring and then dried in an oven.

Fig. 20 shows the possible compounds which may be present in a dried powder after treatment with lead nitrate as activating agent, and sodium oleate as wetting agent.

The compounds of Fig. 20b, the original wetting and activating agents, are not attached to the mineral surface except possibly by secondary valence forces. Either lead nitrate or sodium oleate would be present depending on which had been added in stoichiometric excess. These compounds are soluble in water, and except for any part of them held by secondary valence, could be removed from the powder by washing with water.

The water insoluble heavy metal soap, lead oleate (Fig. 20c), a reaction product of lead nitrate and sodium oleate, likewise could be attached to the mineral surface only by secondary valence forces. While such metallic soaps are insoluble in water, they are quite soluble in many organic liquids, and except where held by secondary valence, could be removed from the powder by washing with carbon tetrachloride.

Fig. 20a represents the condition of the surface of a siliceous particle which it had been hoped most of the activating and wetting agent would react to produce. The bond between the lead ion and oleate radical is a covalent bond, which renders the compound insoluble in water. The bond between the lead ion and the mineral surface is an electrovalen

bond which renders the compound insoluble in organic liquids. Consequently, this compound cannot be removed from the surfaces of the particles by washing with water and carbon tetrachloride.

Since it is on water-repellent compounds of the type shown in Fig. 20a, attached to the mineral surface by means of primary valence, that permanent water-repellency of siliceous materials appears to largely depend, it was desirable to determine the contact angle which had been developed on siliceous surfaces by compounds of this type as the result of any given chemical treatment. Even for mineral particles such as those of limestone, where water-repellency appears to depend largely, if not entirely, on compounds of the type shown in Fig. 12 attached to the mineral surface by means of secondary valence, it was desirable to remove all reagents from the system except those which were irreversibly adsorbed on the mineral surface.

All the powders listed in tables 13, 15, and 17, after being treated with the reagents used in each case, were therefore each washed five times with water, using 200 cc each time, and five times with 200 cc of carbon tetrachloride. These washings were alternated, and the powders were thoroughly dried between washings. Each washing consisted of four or five decantations, the wash liquid being heated before each decantation to assist solution. The washings were decanted through a buchner funnel.

Ten grams of each washed, dried powder were then placed in each of four glass tubes of approximately 11 mm inside diameter, containing carbon disulphide, benzene, chloroform, and n-butyl acetate, respectively. Each tube was thoroughly shaken to remove all air and placed in a rack to allow the powder to settle. Readings of the level of the powder in each tube were taken once a day, and the tubes were shaken thoroughly after each reading. This was repeated until three successive readings were the same. The tubes were then emptied, cleaned, and dried, and the sedimentation volumes determined by titrating the tubes to the sedimentation level from a burette.

The sedimentation data, for the various powders and their treatments as given in tables 13, 15, and 17, have been listed in tables 14, 16, and 18, respectively, and have been plotted versus the interfacial tensions against water of the organic liquids in which they were determined, in Figs. 21, 22, and 23, respectively.

Discussion of Results and their Implication Concerning the Use of Soaps in the Oiling of Earth Roads

It was previously pointed out that the slope of the straight line, resulting when the sedimentation volumes of a given weight of a powder in each of a series of organic

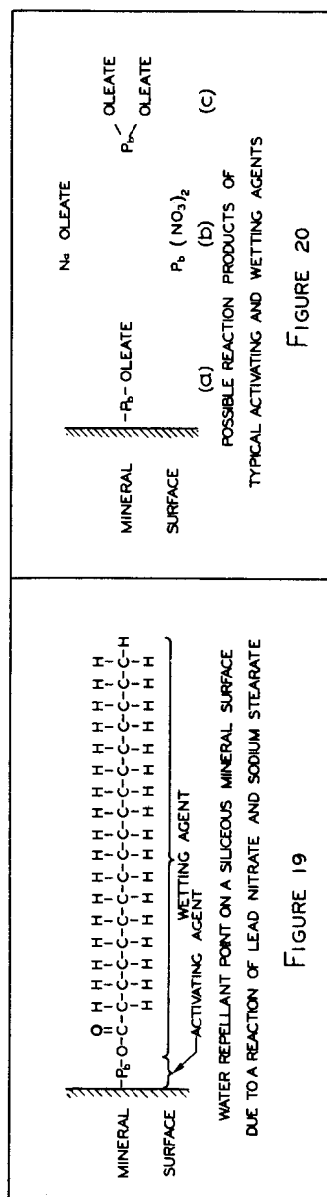


FIGURE 19

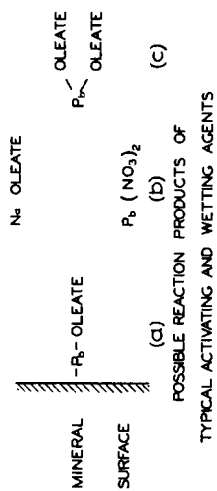


FIGURE 20

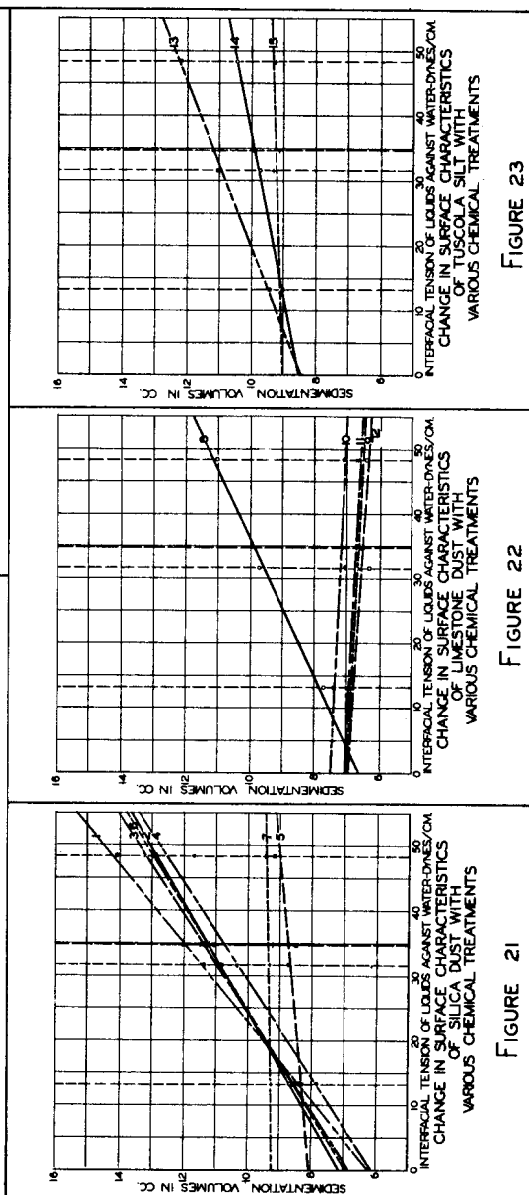


FIGURE 21

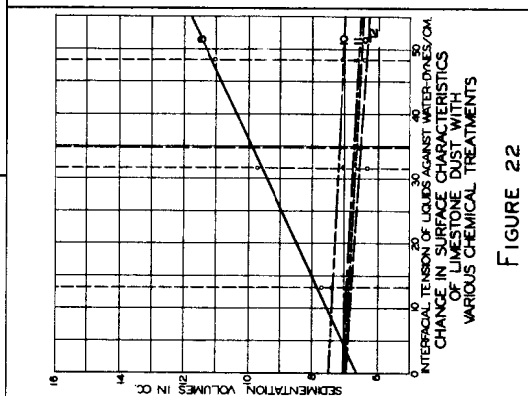


FIGURE 22

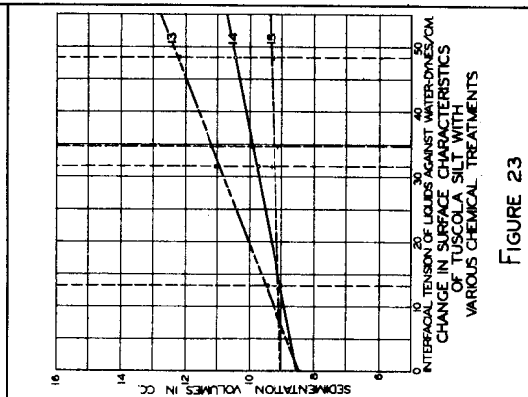


FIGURE 23

liquids are plotted versus the interfacial tensions of these liquids against water, furnishes a measure of the contact angle of water against the particles of that powder, when compared with the slope of a similar line for a powder of the same particle size distribution, shape, and specific gravity, whose contact angle against water is known.

Fig. 21 shows that of the various treatments of the silica powder, a substantial increase in contact angle occurred only for powders 5 and 7, in which lead ion and aluminum ion, respectively, were the activating agents.

From the work of Bartell and Bartell (9), and the relationship pointed out at the beginning of this section, it can be deduced that when the slope of these lines is horizontal, a contact angle of 25° has been developed.

Treatments of the silica powder with either sodium oleate by itself, line 2, or sodium oleate in conjunction with calcium as activating agent, line 3, are unable to develop more than a slight contact angle.

This inability of calcium ion to function here as an activating agent, is further confirmation of results obtained in Part I of this paper, where calcium as an activating agent, with sodium oleate as wetting agent, were unable to bring about the coating of wet siliceous aggregates with bituminous materials.

It was suggested in Part I that this might be due to a relatively small difference in the free energies released when oleate radicles combined with each of the two valences of an adsorbed calcium ion.

Calcium and magnesium ions are the principal divalent cations present in the ionic atmosphere about a soil particle, calcium usually being present in much greater concentration.

The lack of success of oiled earth road surfaces in many localities, appears to be due to the low adhesion tension of the soil for bituminous materials and its high adhesion tension for water.

It has been claimed that the use of soap by itself, greatly increases the adhesion tension between bituminous materials and the soil in the oiling of earth roads, and reverses these adhesion tension relationships. Diagrams appearing in technical literature show one valence of some of the divalent cations present in the ionic atmosphere about a soil particle attached to the surface of the particle, the other valence of each of these cations being attached to a soap radical. These diagrams have been given to show why soap should increase the adhesion tension between a bituminous material and a soil particle.

However, for the usual soil particle such divalent cations could only be either calcium or magnesium, and the results obtained in both Part I and Part II of this paper,

tend to show that in the presence of water and an organic liquid, soap radicals unite with both valences of each calcium and magnesium ion attacked, and the resulting calcium and magnesium soaps appear to be dissolved from the surface of the particle by the organic liquid present. This leaves the particle with its original high adhesion tension for water, so that it remains, or becomes filmed with water. (It is possibly not necessary to point out, that in the oiling of earth roads, the three phase system water-soil-bitumen is involved and not the simpler two phase system soil-bitumen, since surface water is present as a result of rain, snow, etc., and underground water is present due to capillarity, seepage, etc. Water may also be present due to the process used for incorporating the bitumen with the soil.) Consequently it would appear that the use of soap alone would not be likely to appreciably increase the adhesion tension between the usual soil and a bituminous material under normal atmospheric and subsurface, or other moisture conditions.

The results obtained from treating pure silica with calcium chloride as activating agent, are likely to be typical of the results to be expected from the use of soap by itself with most soils in the oiling of earth roads, at least with soils having an intermediate or high silica sesquioxide ratio, since the silica portion is the seat of almost the whole of the base exchange capacity of the mineral fraction of soils.

While it might be expected that the aluminum and iron ions in the mineralogical structure of soil particles should be available for functioning as natural activating agents for these, and consequently should be able to bring about the formation of a water-repellent film when soap was added, there is no evidence to date that this occurs to any material degree. Soap by itself was unable to bring about the coating of wet aggregates such as crushed feldspar, crushed granite, and natural gravels, with bituminous materials in the studies reported in Part I. All of these materials contain iron, or aluminum, or both, in the crystal lattices of the minerals of which they are composed.

Also there is no material flotation of feldspars by soap alone, an externally supplied activating agent being required. It is significant that lime feldspars are more floatable than the potash or soda feldspars upon the addition of soap alone (12), which would suggest that any floatability feldspars possess, depends more on their calcium content than upon their content of aluminum. (It should be observed that while there is no reason why calcium ion should not readily function as an activating agent for certain minerals in the water-mineral-air flotation system, it appears to be unable to function as an activating agent in the water-mineral-bitumen system for the reasons which have been suggested in Part I, or for other reasons not yet perfectly understood.)

The inability of the aluminum present in feldspars to form any material water-repellent film about the surface of feldspar particles in a flotation system by the use of soap alone, can only mean that the aluminum ions in the mineralogical structure of feldspar are not materially available for functioning as an activating agent.

Since soils are made up largely of aluminum silicates, and iron aluminum silicates, from a consideration of the evidence just given, it should occasion no surprise to find that the iron and aluminum ions in these silicates also, do not appear to be able to function materially as activating agents (Fig. 23).

It is interesting to note that Reagel (13), from observations made in connection with the oiling of earth roads in Missouri, stated in 1935, that up to that time, advantages from the use of soap in the oiling of earth roads had not been apparent. This practical observation is highly significant in view of the data presented in this paper.

But while the use of soap by itself would appear to be of little value for increasing the adhesion tension between a soil and bitumen in the oiling of earth roads, the advantage to be expected from the use of soap in conjunction with true activating agents, such as lead and aluminum cations, is strikingly illustrated in Fig. 21. For whereas the use of soap by itself (line 2), or the use of soap with calcium ion as activating agent (line 3), confers no material water-repellency on the silica dust, the use of soap with lead ion (line 5) and aluminum ion (line 7) as activating agents, has given the silica a marked water-repellency.

It should be pointed out here, that from a study of the Bartell and Bartell (9) diagram, it follows that if the sedimentation volumes of a given weight of a number of powders of the same particle size distribution, shape, and specific gravity, but exhibiting different contact angles against water, are determined and plotted as in Figs. 21, 22, and 23, the lines whose various slopes represent the various magnitudes of this water contact angle, will have a common point of intersection with the ordinate representing a liquid with an interfacial tension of approximately 13.2 dynes/cm against water (n-butyl acetate).

It is also an experimental fact that the smaller the average particle size for a given powder, other factors being kept constant, the greater is the sedimentation volume of the powder in a liquid, and the steeper is the slope of the resulting line when the data are plotted as in Figs. 21, 22, and 23.

Fig. 21 illustrates this quite well. The failure of the lines to intersect the n-butyl acetate ordinate at a common point is without doubt due to experimental error. Part of this experimental error may be due to error in sampling, that is to failure to obtain samples of identical particle size

distribution, but it is rather likely that it is largely due to varying losses in fines from the different powders as these are put through the washing and filtering processes required for reagent removal, and consequently to variations in the average particle size of the powders.

Fig. 23, like Fig. 21, illustrates the advantage of using an activating agent along with soap when water-repellency of a siliceous material is desired. The data presented are for a natural soil, a buff-colored silt fairly high in iron, known as Tuscola silt. It is found near the Saginaw Bay region of Michigan. Line 13 is from sedimentation data obtained for the natural silt. Unfortunately, it was not put through the process of washing in water and carbon tetrachloride undergone by powders 14 and 15. It is likely therefore, that it contained a greater percentage of fines than these other two powders. Consequently, line 13 intersects the n-butyl acetate ordinate at a higher sedimentation volume than lines 14 and 15, and its slope is steeper than it should be, relative to the lines representing the surface characteristics of the other two powders, for the reasons just given.

Line 14 resulted from treating this silt with soap alone. The powder resulting from the soap treatment showed no material water-repellency, and was more like the original material, line 13, than is at once apparent from Fig. 23, for the reasons given above.

Line 15, when compared with line 14, again emphasizes the advantage to be expected from the use of a suitable activating agent along with the soap. The water-repellency of powder 15 was quite marked.

It should also be observed that in spite of the fact that this Tuscola silt contains appreciable iron, this iron does not appear to be available for activating purposes to any material degree. If it were materially available in an activating capacity, there would not be the marked difference in water-repellency observed in powders 14 and 15 after treatment with identical quantities of soap as wetting agent. This further confirms the observations previously made, that the aluminum and iron ions in the mineralogical structure of soil particles do not appear to be appreciably available for serving in an activating capacity, at least not under the conditions of pH, etc., occurring in the usual soil solutions. It may be however, that the time factor is important here, and that these aluminum and iron ions would demonstrate activating ability if exposed to wetting agent solution over a sufficiently long period of time.

Fig. 22 gives graphically, the results of some work done with limestone dust. Line 8 is for the original limestone which in this case was not put through the washing process. The other lines have resulted from the various treatments of this limestone dust listed in table 15. It is apparent that

each of these treatments has resulted in approximately the same water-repellency, since lines 9, 10, 11, and 12 have approximately the same slope. It should be observed that in contrast to the results obtained with pure silica, soap by itself, calcium ion plus soap, and calcium oleate in a carbon tetrachloride solution, are all equally capable of developing a contact angle of approximately 25° .

It is interesting that glass tubes filled with any of the powders whose surface energy characteristics resulted in a horizontal slope in Figs. 21, 22, and 23 have shown no capillary rise even under a head of 10 inches of water, over a period of several months. This would appear to be due to a hysteresis effect of some kind, which may be relatively permanent, and if so, may be of some practical importance.

The Rôle of Bituminous Materials in Soil Stabilization

It was stated earlier in Part II of this paper that contact angles of from 50° to 121° have been measured by flotation research workers as the result of certain chemical treatments of various mineral surfaces. However, a contact angle of approximately 25° is the largest that the writer has so far been able to develop in a mineral powder.

In all cases, these flotation workers were using relatively large pieces of minerals, since their technique involved the actual measurement of the contact angle on an enlarged photographic image of the contact made by a small bubble or drop of water on the treated surface of a mineral, and for this, relatively large plane surfaces are required. In the work reported on here, on the other hand, the mineral particles all passed a No. 150 sieve.

It is particularly surprising that a contact angle of 102° should have been obtained as the result of treating a calcite surface with sodium oleate by the technique of these flotation workers (6), while approximately 25° is the largest contact angle that the writer has been able to obtain by treating limestone dust with sodium oleate as determined by means of the experimental technique used in Part II of this paper.

It is beyond the scope of this paper to go into the possible theoretical reasons for the apparent large difference between the values of a contact angle observed as the result of the technique employed by these various flotation workers, and that employed by the writer, if as it appears, the two methods actually do give widely different values for the contact angle developed as the result of any given chemical treatment of a mineral surface.

It should be pointed out however, that the technique for the indirect evaluation of contact angles which has been employed by the writer, is based upon the published results of adhesion tension studies carried out over a considerable

period of time by Professor Bartell, and that there are very good experimental and theoretical reasons for believing that the evaluation of the contact angles of mineral powders resulting from the employment of this technique, is reasonably accurate.

While a contact angle of approximately 25° is the largest that the writer has so far been able to develop in a mineral powder, the reagent consumption for this has been at the rate of approximately 20 pounds of activating agent, and 20 pounds of wetting agent, per ton of mineral powder treated, or a reagent cost of from two to three dollars per ton of powder. This would be relatively costly as far as practical application is concerned, for most engineering purposes.

To develop a contact angle of 90° , at which point a soil would have zero capillarity for water, would require a prohibitive amount of these reagents if such a contact angle could be developed by them at all, which to the writer is very doubtful.

One of the principal reasons for the large quantities of reagents required for the development of this relatively small contact angle, is that most of the reagents appear to react not on the surfaces of the particles, but in the spaces between the particles, forming compounds of the type shown in Fig. 20c, which have little, if any ability to develop or increase the contact angle of siliceous materials against water. Judging from the dark color of the first two washings with CCl_4 when lead nitrate and sodium oleate were used as reagents in the treatment of the silica powder, it would appear that possibly most of the reagents added have reacted to form lead oleate (Fig. 20c). This appears to be the principal reason for the relatively large quantities of reagents required for the small contact angle developed.

There is another method of attack on this problem, however, which has promise of developing a contact angle considerably in excess of 25° , and at a greatly reduced reagent cost. This method combines the use of bituminous materials with wetting and activating agents.

In Part I it was pointed out that heavy metal soaps, such as lead oleate (Fig. 20c), when dissolved in bituminous materials, were unable to cause bituminous materials to displace water on the surfaces of wet siliceous aggregate particles. However, upon the addition of a small amount of lead nitrate solution, displacement of the water began to take place. This water displacement became more complete as lead nitrate solution continued to be added, until the total lead and total oleate were present in about the proportions of one equivalent of oleate radicals to two equivalents of lead ions.

It should be apparent from this that in the presence of a bituminous material, the lead oleate present in the spaces

between the siliceous mineral grains when water solutions only, of lead nitrate and sodium oleate in optimum proportions were used, would be dissolved in the bituminous material, and by reacting with the free lead nitrate present, would be converted into the required compound (Fig. 20a), attached to the mineral surface by primary valence thereby creating the water-repellent points required for developing a permanent contact angle against water.

In this case, however, each mineral particle would also be coated with a film of bitumen, and the contact angle developed would be that between the bitumen film and water, rather than between the hydrocarbon groups of the wetting agent attached to the mineral surface and water.

Consequently, since the contact angle developed would depend very largely or wholly on the bitumen, the wetting and activating agents would now be added largely for the purpose of making the adhesion tension of the surfaces of the soil particles greater for the bitumen than for water, in order that the soil-bitumen mixture would be thermodynamically stable against any uncoating tendency of water.

Qualitative tests have shown that for natural Michigan silts, the reagent requirement per ton of silt to make the adhesion tension of the silt greater for bitumen than for water, is several times less than the amount of the same reagents required to develop a solid-water-air contact angle of 25° in these silts.

As for the magnitude of the contact angle which the bituminous films about these soil particles would exhibit against water, no measurements are available so far as the writer is aware. It is unlikely that the contact angles of water on films of present-day bitumens would be greater than from 70° to 80° judging from the structure and composition suggested for bitumens. The contact angles exhibited by a great many bitumens might even be considerably smaller than this. On the other hand, for bitumens of the Nujol type, a contact angle of 105° , the contact angle between solid paraffin and water, might be possible. It is very likely that those bitumens having a high natural adhesion tension for soils, would exhibit a small contact angle against water, for since both soils and water are polar materials, a high affinity for one, in general, indicates the possibility of a high affinity (small contact angle) for the other.

It should be apparent that for the stabilization of soils by this method, almost any liquid petroleum product or other hydrocarbon liquid material, possessing water-repelling properties, such as crude oil, refinery residues of various types, tars, etc., would serve. Under conditions of abrasion or wear, and where stability was important, however, bitumens

meeting well defined specifications, such as cut-backs, flux oils, powdered bitumens, etc., would be required.

If the introduction of a bituminous material in the interest of reagent economy is essential or necessary for the development of a high contact angle between a soil and water, it appears to be a necessity for another reason.

If a contact angle of 90° or more could be developed between soil particles and water, the soil would be so water-repellent that no capillary water could be present. The water films, which are essential for the coherence of inert materials, would be absent, giving a cohesionless, dusty, mass which would present construction difficulties. It would, therefore, be necessary for construction purposes, to add small quantities of oils or bitumens to stabilize such water-repellent soils.

The Effect of Conditioning Agents

Some tests with special reagents which do not act either as wetting agents, or activating agents, but increase the effectiveness of these have been made. Following flotation terminology these may be called "conditioning agents."

The following observations will illustrate the effect of these when coating wet siliceous sands with bituminous materials by the addition of wetting and activating agents.

3 cc of a 0.05M sodium carbonate solution, caused manganese chloride to function as a satisfactory activating agent when the aggregate was a pink feldspar which could not be coated by bitumen while wet by the use of the manganese salt and wetting agent alone.

Two different granites (one of these used for table 3) were poorly coated by bitumen while wet, using copper chloride as activating agent. The addition of 1.0 cc of 0.05M sodium silicate in each case gave perfect water displacement. Sodium silicate has a stripping effect, however, when used in larger quantities.

The trivalent phosphate ion appears to be detrimental in all quantities, and causes rapid and practically complete stripping.

The tetravalent ferrocyanide ion also has a decided stripping action, although not to nearly the same degree as phosphate ion.

With lead and copper ions as activating agents, coating is very poor below a pH of about 4.0 and above a pH of about 12.0.

Using aluminum and iron ions as activating agents, coating by bitumens is very unsatisfactory above a pH of 8.0 and below a pH of about 4.0.

Even with small alkalinity there is considerable tendency for the bitumen to emulsify in these mixtures due to the presence of the hydroxyl ion.

The most satisfactory pH appears to be near neutrality, or in a range of approximately 6.0 to 8.0.

In spite of the stripping action of phosphate ion and excess silicate ion, it would appear possible on theoretical grounds at least, that through the development of the proper technique, these ions could be made use of to increase the base exchange capacity of a soil where this was desirable.

Conditioning agents appear to be necessary or desirable in many cases to effect a change in either the base exchange, or pH, or both, about the surfaces of wet particles it is desired to coat with bitumens through the action of wetting and activating agents.

The Nature of the Adsorption of the Water-Repelling Activating-Agent-Wetting-Agent Reaction Products

The experimental results which have been obtained in Part II of this paper, tend to confirm the conclusion arrived at in Part I, that in the presence of water and an organic solvent, water-repelling reaction products of wetting and activating agents must be adsorbed on the mineral surface by means of primary valence in the case of siliceous minerals, if permanent water-repellency by means of these is to be obtained.

While the problems involved in both Parts I and II have centered around the creation of water-repellency on the surfaces of mineral particles, the experimental technique used for determining this water-repellency has been decidedly different in each case.

In the discussion of Fig. 20 it was pointed out that compounds like sodium oleate (Fig. 20b), present only if in stoichiometric excess over any activating agent present, and like lead oleate (Fig. 20c) could not be expected to confer any water-repellency on a mineral surface unless adsorbed by secondary valence forces.

Line 2, Fig. 21, indicates that sodium oleate by itself is unable to confer any material water-repellency on a silica surface. Due to the absence of cations on the surface of pure silica with which the soap could form insoluble compounds, sodium oleate could only be adsorbed by secondary valence. Since any sodium oleate which may have been so adsorbed, was for all practical purposes completely removed by a few washings with water and carbon tetrachloride, it was evident that

the adsorption of soaps by silicates through secondary valence is of only minor importance compared with their adsorption in conjunction with suitable activating agents by means of primary valence, lines 5 and 7.

In order to demonstrate experimentally that the adsorption of compounds of the lead oleate type (Fig. 20c), on silica surfaces is also of minor importance, calcium oleate and lead oleate, corresponding in quantity to that shown in table 13 for powders 4 and 6 respectively, were dissolved in carbon tetrachloride and added to 100-gram lots of dry silica powder. Due to the nature of its solvent action, only compounds of the type shown in Fig. 20c could be present in this carbon tetrachloride solution, and so activating agents of the nature of lead nitrate would be absent. After standing for a day, and then being dried in an oven, these were put through the usual washing process, and their sedimentation volumes then determined. Line 4, Fig. 21, indicates the result of the calcium oleate treatment, and line 6, of the lead oleate treatment. It will be observed that no material water-repellency has been developed by either of these treatments. Tests conducted in a similar manner have shown that aluminum oleate dissolved in carbon tetrachloride is no more effective for developing water-repellency in silica dust than lead oleate or calcium oleate.

Lines 5 and 7 on the other hand, indicate that lead and aluminum ions as activating agents respectively, together with sodium oleate as wetting agent, when reacted in the required proportions on the surfaces of silica particles, are able to develop appreciable water-repellency. Any water-repelling reaction products of these reagents which were held on the surfaces by secondary valence, would have been removed by the washing process as shown in the previous paragraphs. Since the treated silica powders are still water-repellent after the process of washing, lines 5 and 7, it follows that the reaction products still effective must be held to the surfaces of the particles by other attractive forces than those of secondary valence. It appears very reasonable that these other attractive forces are those of primary valence, as illustrated in Fig. 20a.

Silica dust treated with water solutions of calcium chloride as activating agent, and sodium oleate as wetting agent, shows no more water-repellency, line 3, than is obtained by treating the silica with a carbon tetrachloride solution of calcium oleate, line 4. This is further evidence of the inability of calcium ion to attach water-repelling reaction products of itself and wetting agents to a silicate surface by means of primary valence, and so to function as a true activating agent.

Since there might be some doubt as to whether carbon tetrachloride solutions of lead oleate, aluminum oleate,

calcium oleate, etc., furnished the conditions under which adsorption of these compounds on the surfaces of mineral particles could occur, 100-gram lots of a limestone dust were treated with carbon tetrachloride solutions of lead oleate and calcium oleate, table 15, powders 11 and 12. After standing for a day with occasional stirring, they were dried and then put through the usual washing process. Their sedimentation volumes were determined, and these are plotted in Fig. 22 as lines 11 and 12, respectively. It may be observed that these treatments gave as water-repellent powders as the more usual treatment of the limestone dust, first with activating agent solution (lead nitrate), then with wetting agent solution, line 10. Consequently, it may be inferred that under the conditions being considered here, adsorption by a mineral surface from carbon tetrachloride solution will take place if the compounds in solution are capable of being adsorbed, and with the same degree of irreversibility as if the compounds had been adsorbed from a water solution.

Incidentally, this latter test appears to further confirm the tentative conclusion presented in Part I, that the adsorption of the water-repellent reaction products of activating and wetting agents by limestone particles, occurs largely, if not entirely, through the exercise of secondary valence forces.

Limitations of a Physical Explanation of the Adsorption Phenomena Considered in this Paper

The experimental results which have been given in this paper are capable of furnishing a very good example of the possible physical adsorption effects due to the presence or absence of dipole moments in the molecules making up the various phases of a system, or to other physical factors, and also, what is equally important in the present case, of the inability of explaining all of the adsorption phenomena involved, on the basis of dipole moment or other physical effects. A brief discussion is appended in the following paragraphs to bring this out.

In certain molecules, or in parts of certain molecules, the centers of gravity of the electrons and protons which make up the atoms in the molecule, do not coincide. This separation of the centers of gravity of these small elementary charges, gives rise to a dipole moment whose magnitude is equal to the product of one of the resultant charges multiplied by the distance between them. A molecule containing a dipole moment, or even an ion, may induce dipole moments in molecules near it which do not normally have dipoles, and molecules containing permanent dipoles may orient themselves with respect to each other so as to either increase or decrease the dipole moment in each. Consequently, the situation in a system containing molecules having dipoles is not

necessarily predictable and may become quite complex.

The presence of a dipole moment in a molecule may set up certain strong unsymmetrical fields of force outside the molecule, the conception of which, Debye, Smythe, Williams, and others, have found useful in furnishing explanations for molecular structure, adsorption, orientation, etc.

Anything but the most general discussion of the possible effects of dipoles in molecules is out of place here. It might be pointed out by way of example however, that water, whose molecules contain a dipole moment, is a liquid at normal temperatures due to the strong attraction between its molecules because of the dipoles they contain, while hydrogen sulphide (which may be considered to be derived from water by substituting a sulphur atom for the oxygen atom of the water molecule) whose dipole moment is approximately one half that of water, is a gas due to the much weaker attraction between its molecules.

The force of attraction between ions and charged particles varies inversely as the square of the distance between them, the attraction between dipoles varies inversely as the fourth power of the distance between them, and the weaker van der Waal's forces vary inversely as much higher powers of the distance. Consequently, in water solutions the forces between ions are stronger than those between dipoles, and the forces between dipoles are stronger than the van der Waal's forces. It should also be apparent that when only molecules are involved, the strongest intermolecular forces are between those molecules possessing dipoles.

Il'in (4) has summarized the effects of molecular forces at the boundaries of different phases due to the presence of dipole moments in the molecules of each phase as,

(1) When the dipole moment of an adsorbent is greater than that of a polar solvent in which it is immersed, the adsorbent is lyophilic. In this case, a solute dissolved in this polar solvent will be adsorbed if its dipole moment is greater than the dipole moment of the solvent.

(2) When the dipole moment of an adsorbent is less than that of a polar solvent in which it is immersed, the adsorbent is lyophobic. In this case, a solute will be adsorbed if the dipole moment of the solute is less than the dipole moment of the solvent.

These relationships are reversed if the solvent is non-polar.

For the problem of the coating of wet mineral particles with bitumens which is being considered in both Part I and Part II of this paper, consider the mineral particles as the

adsorbent, the water as the polar solvent, and the bitumen as the solute.

It has already been stated that the minerals composing ordinary aggregates and soils are polar minerals. No data are available which give the dipole moments of the molecules making up these minerals, but since they are lyophilic to water, their dipole moments must be greater than the dipole moment of water according to Il'in's first generalization.

Since bitumens are essentially hydrocarbon materials, it follows that their dipole moments are much less than that of water. Consequently, from Il'in's first generalization, a bituminous material will not be adsorbed by a wet mineral aggregate - a well known fact.

Now however, consider the case where the particles of the same mineral aggregate have been coated with a film of hydrocarbon groups, Figs. 5b, 7b, and 19. (There is no necessity at this point to consider the mechanism, chemical or physical, by which this hydrocarbon coating has been achieved.) The dipole moment of these hydrocarbon groups is much less than that of water, and consequently, the dipole moment of the surfaces of the aggregate particles has been made less than that of water.

Applying Il'in's second generalization, it is obvious that the aggregate (adsorbent) is now lyophobic, and this second generalization indicates further, that in the presence of water, this aggregate should now adsorb the bituminous material. The many hundreds of mixtures in which the aggregates were coated while wet during the investigation reported in Part I, serves to confirm this second generalization.

Thus far, the interpretation of the observed phenomena on the physical basis of dipole moment effects is in agreement with experience.

On the basis of the results obtained in this paper, however, a simple explanation, on the basis of dipole moment or any other strictly physical effects, of the formation of the water-repellent hydrocarbon films on the surfaces of the mineral aggregate particles through the use of wetting and activating agents, Figs. 5b, 7b, and 12, appears out of the question.

In spite of the rapidly increasing knowledge of the inner structure of the atom, and consequent gradual breakdown of the old boundaries between strictly chemical and strictly physical phenomena, chemistry and physics are still separate sciences. Consequently, it is still justifiable to distinguish a reaction between molecules as chemical or physical, on the basis of whether or not a sharing of electrons between atoms of the molecules has taken place, provided a double decomposition reaction, which has always been considered adequate evidence of a strictly chemical reaction, does not occur between the molecules. However, while chemical and

physical reactions between molecules may be distinguishable on this basis, it is extremely difficult, because of the incomplete state of present knowledge, to ascertain in all cases whether or not such a sharing of electrons has occurred. This is particularly true of adsorption phenomena.

There is no general agreement yet among flotation research workers, as to whether the water-repellent films created on the surfaces of mineral particles in flotation systems by the use of collecting (wetting) and activating agents, are held to these mineral surfaces by chemical or physical forces (14), (15).

In view of the fundamental differences existing between a flotation system and the water-aggregate-bitumen system being considered here, it is almost obvious that theoretical reasoning applicable to the former, may not be applicable to the latter system.

The writer fails to see however, for the water-aggregate-bitumen system, how it is possible to explain on the basis of dipole moment effects, or on any other strictly physical basis, the ability of certain polyvalent cations like lead and aluminum to function satisfactorily as activating agents, and the inability of the divalent alkali earth metal and magnesium cations, and the monovalent silver cation, to serve in an activating capacity, when used with various wetting agents for creating a water-repellent film about the particles of siliceous aggregates. Nor does it seem possible to explain on a physical basis the difference in the optimum proportions of activating and wetting agents which appear to be required by siliceous and limestone aggregates, nor why almost any polyvalent cation appears to function satisfactorily as an activating agent for limestone aggregates, while there are limitations on these cations which are suitable as activating agents for siliceous aggregates.

In contrast to the inability of explaining these latter, various, experimentally observed effects, on a strictly physical basis, it has been shown in Part I, and also in the immediately preceding section of this paper, that these various *effects can be quite simply explained on a strictly chemical basis.*

Consequently, it is reasonable to assume for the present that,

(1) The water-repellent, bitumen-attracting, film formed on the surfaces of wet aggregate particles by the use of wetting and activating agents is the result of a chemical reaction between the activating and wetting agents adsorbed on the wet mineral surfaces.

(2) The products of this chemical reaction may be attached to the mineral surface by either a chemical

or a physical adsorption (apparently largely chemical for siliceous aggregates, and physical, or largely so, for limestone aggregates).

(3) The attachment of the bitumen to the water-repellent films created by these reaction products is physical.

CONCLUSIONS

A. Theoretical

1. It has been shown how mineral powders, including a natural silt soil, can be rendered capillary repulsive to water.

2. Water solutions of activating and wetting agents by themselves, in any reasonable quantity, appear unable to develop a contact angle much greater than of the order of 25° between mineral particles and water.

3. A marked hysteresis effect, relative to capillary rise, has been noted when a contact angle of approximately 25° has been developed by means of these reagents, which might be of some practical value.

4. The data of Part II support the conclusions drawn in Part I that,

a. Water-repelling reaction products of wetting and activating agents appear to be strongly adsorbed on siliceous surfaces through the exercise of primary valence.

b. Water-repelling reaction products of wetting and activating agents capable of exercising only secondary valence are incapable of being strongly adsorbed on siliceous surfaces in the presence of water and organic solvents.

c. Water-repelling reaction products of wetting and activating agents are adsorbed on limestone surfaces chiefly, if not entirely, through the exercise of secondary valence forces.

5. The use of bituminous materials, or other hydrocarbon oils appears to be necessary for making soils highly capillary repulsive to water for three principal reasons:

a. To obtain a sufficiently high contact angle.

b. For the sake of reagent economy.

c. For the purpose of supplying the cohesion in water-repellent soils, that water films supply in ordinary soils.

6. Data and theoretical reasons have been given as to why the use of soaps by themselves are likely to be of little, if any, value in the oiling of earth roads.

It has been shown that the use of soaps in conjunction with certain activating agents, however, may be expected to greatly increase the adhesion tension between soil particles and bituminous materials.

B. Practical

As in Part I, due to the lack of any field tests whatsoever, only very tentative conclusions as to the practical application of these research results can be drawn. It is almost a platitude to say that the possible practical adaptation of these results on any construction project will depend on economic considerations. The cheapest materials and construction methods which will give a subgrade of sufficient stability to support a smooth surface of the type required for traffic, and at the same time will resist frost and water action, will be used, if possible.

Here also it is necessary to point out, however, that when used in combination with bituminous materials, the quantities of reagents required, which have varied in cost from about twenty-five cents to about one dollar per ton of soil treated on a laboratory scale, at least makes this a border line method when compared with present standard methods from the point of view of initial cost alone, in many cases where it is impossible or undesirable to use the soil on the location for the subgrade. Any reduction in reagent requirements through the economies of plant-scale operation, or through the discovery of more efficient reagent combinations, would permit this method to compete still more favorably with the present standard methods.

No other method, unless capable of effecting results similar to the method outlined here, in which the surfaces of soil particles are made water-repellent due to the adsorption of water-repellent substances by the exercise of either primary, or secondary valence forces, or both, is capable of making a soil permanently capillary repulsive to water. This applies even in those cases where certain bitumens have been used without the addition of special reagents for stabilizing soils.

As to whether, in order to make a subgrade completely insusceptible to frost and water action, the subgrade soil would have to be made water-repellent to the depth of the frost line, or to a certain fraction of this depth, or

whether a less expensive type of construction involving a membrane of water-repellent soil placed at some depth below the grade line, joined possibly to a water-repellent veneer on the shoulders, together with an impervious top, would function satisfactorily, is a problem in design and construction technique which will have to await experimental work in the field.

Keeping these limitations in mind, the following possibilities resulting from the use of this method are at least worthy of consideration.

1. Any soil material which was made sufficiently water-repellent by this or a similar process should function satisfactorily as subgrade material. This applies even to frost-heave and frost-boil soils, which at the present time are generally excavated and replaced by granular materials. The engineer would thereby become much more independent of the nature of the soil profile in the selection of subgrade materials.

2. Well designed highway surfacings placed on well consolidated subgrades of such water-repellent soils should remain as smooth as it is possible for road surfaces to be constructed by mechanical equipment. The differential heaving and settling of road surfaces occurring at the present time due to fluctuating or differentially increasing moisture content of the subgrade would be largely eliminated.

3. The spring "break-up" could be greatly reduced or eliminated for subgrades constructed of soils made capillary-repulsive to water. This would eliminate the necessity for the present load limiting regulations on the motorized transportation of freight, which must now be enforced whenever the subgrade becomes waterlogged.

4. Soil mechanics as applied to highway design would become a more exact science for those highways in which the soil subgrade was water-repellent. The maximum bearing capacity for design (the minimum bearing capacity of the subgrade) could be established by bearing capacity measurements in the summer when the subgrade was at its highest temperature.

5. The lack of success of oiled earth road surfaces in most localities today, appears to be due to the low adhesion tension of the soil for bituminous materials and its high adhesion tension for water. The process

which has been outlined here, by reversing these adhesion tension relationships, would make oiled earth stable in the presence of water as far as any stripping action is concerned.

By this process therefore, using the soil materials in situ, and with some care in the design of these oiled earth surfaces, it would appear as though many thousands of miles of unimproved and market roads could be provided with all-weather surfaces where this is not now economically possible using the materials required by present construction technique.

6. Soils which have been made capillary-repulsive to water should find a place in the construction of water-tight earth dams, the revetment of levees, and in a number of other engineering fields where water-repellency is essential.

7. In conclusion, it should be pointed out that the use of bituminous materials as outlined here, offers greater possibilities as an outlet for the ever increasing quantities of petroleum refinery residues than any other engineering use which can be made of these materials.

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LITERATURE CITED

1. Adam, N. K. The Physics and Chemistry of Surfaces, p. 193, Oxford University Press (1930).
2. Adam, N. K. Ibid, p. 213.
3. Wark, I. A., and Cox, A. B. Tech. Publ. No. 461, A.I.M.E., p. 30.
4. Il'in, B. V. Chemical Abstracts, 26, 15 (1932).

5. Wark, I. A., and Cox, A. B. Loc. cit., p. 20.
6. Siedler, P. Kolloid Zeit., 68, 92 (1934).
7. Bartell, F. E., and Walton, C. W. J. Phys. Chem., 38, 503 (1934).
8. Mack, Charles J. Ind. and Eng. Chem., 27, 1500 (1935).
9. Bartell, F. E., and Bartell, L. E. J.A.C.S., 56, 2205 (1934)
10. Gaudin, A. M. Flotation, p. 361, McGraw-Hill Book Co., Inc. (1932).
11. Gaudin, A. M. Ibid, p. 33.
12. Gaudin, A. M. Ibid, p. 381.
13. Reagel, F. V. Proceedings Second Annual Montana Bituminous Conference, pp. 237-8 (1936).
14. Gaudin, A. M., Dewey, F., and Duncan, W. E. Transactions, A. I. M. E., 112, 318-47 (1934).
15. Taggart, A. F., del Giudice, G. R. M., and Ziehl, O. A. Ibid, pp. 348-81.

DISCUSSION OF MR. McLEOD'S PAPER

DR. WINTERKORN: Concerning the use of alkali-soaps in connection with bituminous materials a typical mistake appears to have been made and remade in different directions. This mistake is improper generalization. We have found and published beneficial results of soaps in the bituminous stabilization of definite soils the characteristics of which were given in the respective reports. These results were unduly generalized by the readers and soap appears to have been regarded by them as a cure-all up to the unavoidable disillusioning. Now the pendulum is swinging back and Mr. McLeod is condemning beautifully and sweepingly the use of soap. Mr. McLeod's experiments were conducted on quartz-sand. If the surfaces of this were absolutely clean from mineral matter, nobody who knows anything about the crystal make up of quartz and about the physical and chemical character of bituminous materials would expect any beneficial results on the adhesiveness of the bitumen from the use of soap in this case. (Neither can it be seen from the crystal structure of quartz how it could possibly have base exchange

properties.) Obviously, the effect of soap will be different for different mineral surfaces and will be either beneficial, neutral or even detrimental according to the chemical composition of these surfaces. Since the chemical character of soil materials is a function of the parent materials and of the climatic forces which have been acting on them, the effect of soap treatment is variable even in earth oiling. Consequently, all actual construction projects should be preceded by laboratory experiments made on test specimens consisting of the mineral materials to be used and of the bituminous materials and admixtures under consideration.

MR. DOW: Gentlemen, I am glad to hear this paper this afternoon; I think it is a great step in the right direction. I have been working with aggregates and soils for a long time, but in more of an experimental than a scientific way. I find that the author struck upon ferric chloride as being one of the best reactivating agents we could find. We also found that if we washed some silicas with hydrochloric acid it rendered them active to bitumen, and from this we tried ferric chloride and find it the best of a number of other reagents tried. Since Mr. McLeod has given results on a number of reagents and the scientific method of estimating their activating properties, this will greatly simplify the study of aggregates. The study of various activating agents on different soils will be of great aid in the stabilization of these soils with asphalt. In the line of asphalt pavements you should remember that they are generally composed of about ten per cent bitumen and ninety per cent aggregate, and therefore the aggregate is the most important ingredient to study.

MR. NICHOLSON: While I have been pleased at this meeting with the reception and recognition the subject of adhesion has received, I believe I was one of the very first in the Association to bring this matter up. I was rather ridiculed five years ago on presenting my ideas and it was thought at the time that they were more or less a dream. I presented the washing test at that time, but I knew over six years ago what has been brought out here this afternoon. There are one or two new points that have been brought out in the paper by Mr. McLeod pertaining to the question of soaps, and of course the conditions he worked with are different from those I worked with. I had been working with rock asphalt and not applied asphalt only, and at the time I started, knew that my test for adhesion would not be any good unless I found some good and some bad samples. I am sure Mr. Hinkle of the Kentucky Rock Asphalt Institute is going to be very much interested to hear this; the reason why I became interested in adhesion, was that in examining the rock asphalt

from Kentucky, I found certain samples that showed a high degree of adhesion, and the adhesion seemed to increase with age. You recall that in the first paper I read, I stated that the first material did not seem to be very good, but as the substance aged, the adhesion increased. So I reasoned that there must be something in the character of the surface. There must be something present to account for this condition. So we extracted all the asphalt from the surface, and having a pH apparatus available, I found that all the aggregates from Kentucky Rock Asphalt that showed a good deal of adhesion had a low pH value, a value of about four. The first thing that comes to mind on finding a low pH is that some acid must be present. So I mixed up some silica filler and silica sand and added some sulphuric acid to it, prior to the addition of the hot asphalt. I found that the adhesion was much poorer than I ever saw before, in fact the sulphuric acid seemed to make the asphalt come off the grains. Then I happened to think of the acid metallic salts, the trivalent ones, the iron and aluminum ones principally. So we chemically analyzed the surfaces of the rock asphalt mineral grains and found them to contain iron and aluminum sulphates. Then I went ahead and added iron and aluminum sulphate to the silica aggregate as it appears in the Kentucky Rock and found we could exactly duplicate the adhesion conditions in Kentucky Rock. However, in the laboratory, we found it did not seem to do it unless we made a small addition of fatty acid pitch to the asphalt before spreading it on the aggregate. For some time we believed this addition of pitch was necessary. On going out into the asphalt plant and mixing on a large scale, we found that the addition of the fatty acid pitch was not necessary and that the asphalt stuck to the sand grains in the presence of only the trivalent metallic ions. That is the difference between my findings and those of Mr. McLeod, and I think they will be of interest to you.

DR. MULLINS: I would like to add a comment here. You know in the application of chemistry to bituminous construction, this paper this afternoon dealt with the principle known in the dye industry as "fixing." Many of the dyes we use in coloring goods will not fix the goods and it is rather interesting to note that the same materials discussed today are often used as fixers in the dye industry. I notice the experiments were carried out with twentieth molar solutions. You will get entirely different results if you vary the molarity of your solutions due to the different ionization contents. Some of the salts might, with different concentration, give good results, at least they will vary a great deal.

I will illustrate by an example from the drug industry.

During the war they needed drugs, which manufacture started by nitrating the benzene ring compounds. The reaction was slow. They then increased the nitric acid concentration and it still did not work. Someone looked up the ionization constant and found that ten per cent would ionize twice as well as fifteen, and so on; so they used that ratio and got their product immediately.

Our next step would be then to determine the ionization constant of these various salts and apply that to the particular chemistry of fixing. The use of the primary, secondary, and tertiary ionization constants will eliminate untold work of the kind discussed. That application is logical although it may not be practical due to cost. The fact that the ionization constant is a factor was illustrated by the reaction on the addition of lead salt when an oleate ion was used as a fixer. This is a factor we cannot overlook, because fixers used in this form become permanent and you will find that the union is a permanent union and it will be very important in coating crystalline aggregate.

All it would be necessary to do in order to find the correct fixer would be to determine the electrical potential on the aggregate and to match that by the proper ionic potential as determined by the character of the ion itself and the ionization constant which would free that ion having the correct potential to form the permanent bond between the aggregate and the fixer. In other words, if we are going into coating of aggregate with asphalt by means of fixers, we should make a more intensive use of the electro-chemical literature and data available. In many cases the reaction of different salts at different concentrations could be determined by a survey of data found in chemical literature without any experimentation whatsoever being necessary. Were the relationship between the fixer and the aggregate thus solved, the next step would be the relationship between the fixer and the asphalt, which might possibly vary between different asphalts.

McLEOD [By Letter]: It is to be regretted that no pre-prints of the paper were available for those who wished to take part in the discussion. Because of the length of the paper, it was not possible to present much more than a general outline in the brief time allotted. Many of the details which had to be omitted in presentation would have no doubt clarified some of the points which have been raised in the discussion.

Most of the points brought up in the discussion by Dr. Winterkorn have been quite adequately treated in the paper itself. It should be observed that while the writer, on the basis of the experimental data presented, has questioned the value of soap when used by itself in the oiling of earth

roads and for increasing the adhesion tension between siliceous materials and bitumens, the advantages to be expected from soap and other suitable organic compounds when used in conjunction with suitable activating agents have been emphasized throughout the paper.

The paper discloses also that the investigation covered a wide variety of mineral aggregates and was not limited to quartz or silica materials alone. For none of those investigated, with the exception of certain limestone materials, did soap by itself appear to be able to materially increase the adhesion tension between the mineral material and bitumen under the test conditions used.

While it is quite true that pure quartz and pure silica have no base exchange capacity, articles by many writers indicate that the surface of a quartz or silica particle in water, or even in moist air, is composed not of silica, but of silicic acid due to hydration of the surface layer of quartz or silica. This silicic acid coating gives the quartz particle base exchange properties which have been used by flotation research workers to explain certain flotation phenomena such as the activation of quartz by heavy metal cations, and the formation of silica slime coatings on mineral sulphide particles in flotation circuits leading to the loss of these particles in the tailings.

The writer would like to add his own unqualified endorsement to the last sentence in Dr. Winterkorn's discussion, and if amending it at all would only make it more emphatic.

Mr. Dow and Mr. Nicholson both mention having observed increased adhesion tension between an aggregate and bitumen upon the addition of a soluble salt containing a trivalent cation. These trivalent cations are very likely adsorbed on the surfaces of these aggregates by means of a base exchange reaction. This adsorption would effect a large reduction in the silica sesquioxide ratio of the immediate surface layer. Several writers have reported increasing adhesion tension between bitumens and mineral aggregates, as aggregates of decreasing silica sesquioxide ratio were used. The actual adsorption mechanism resulting in the increase in adhesion tension due to this does not yet appear to be well understood.

As Dr. Mullins has pointed out, the activating agents whose function in the problems considered in this paper has been to act as an intermediary for attaching the wetting agents to mineral surfaces, would in the dye industry be known as fixers or mordants. However, due to the fundamental differences in structure between minerals and textiles, it would be hazardous to say that this relationship amounts to more than an analogy, since the most satisfactory mordants would not necessarily be the most satisfactory activating agents, and the reaction mechanism between dyes and mordants in some cases at least, is of a different nature from that

between the wetting and activating agents considered in this paper.

In connection with the use of ionization constants, it should be observed that these can be calculated with reasonable accuracy only for dilute solutions of materials like acetic acid which have very small ability to ionize in solution. Many electrolytes are considered to be completely ionized at all concentrations, and for these the term ionization constant would have no meaning. For concentrated solutions of all electrolytes, and for even dilute solutions of strong electrolytes, the ion concentrations can be only approximately determined due to interionic attraction, removal of solvent by solvation of ions and molecules of the electrolyte, etc.

Also, regardless of the magnitude of the affinity of an ion for a mineral surface, the law of mass action shows that ions with a high affinity for a mineral surface, can be largely displaced by ions having a much lower affinity for the surface, if the latter are present in sufficiently great concentration.

Because of the desirability of using the mass action constant in its various forms as a true constant, and because of the impossibility of determining the actual concentration of ions in many systems, investigators usually prefer to use the thermodynamic method of attack for obtaining quantitative data concerning the possibility of reactions of the type considered in this paper. This involves the use of the thermodynamic concepts of the activity of ions in solutions, free energy, heat content, entropy, etc. In many cases also, the concepts of chemical kinetics must be introduced, because in spite of the fact that thermodynamics can show whether or not a reaction is possible, because of the high activation energy which may be required by the reactants the reaction may proceed far too slowly under a given set of conditions to be of any practical value. Chemical kinetics show that in many practical cases the predominating product is the one produced by the fastest reaction, and not the one which would be expected on thermodynamic grounds, although the latter product would always result if the time element were made sufficiently long.

It should be observed that there would appear to be no particular necessity for determining the relationship between the "fixer" (activating agent) and the asphalt as the problem has been treated in the paper. The activating agent merely serves in some way to tie the wetting agent to the mineral surface, and any consequent relationship involved is primarily between the wetting agent and the bituminous material.

The relationship between bitumen and activating agent would, however, apply to the cases described by Mr. Dow and Mr. Nicholson.