

Improvement of Asphalt-Stabilized Fine-Grained Soils with Chemical Additives

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The object of this investigation was to determine the effects of selected chemical additives upon the strength and water-resistance of asphalt-cutback-stabilized soils. The majority of the work was devoted to studying the effects of fatty amines and phosphorus pentoxide, in conjunction with asphalt, on soil stability; variables studied included soil type and/or plasticity, Additive and Asphalt Concentration, Molding Water Content, Curing and Ageing Conditions, Asphalt Origin and Hardness, Cutback Composition and Solvent.

Treated soils were molded and statically compacted under controlled conditions, cured for specified periods in air with controlled relative humidity, and totally immersed in water for prescribed periods. Samples thus prepared and conditioned were tested in unconfined compression, and their densities and volatiles contents measured by standard procedures.

Salient results of this study were as follows:

1. Successful stabilization (evidenced by development of substantial wet compressive strength within one day) was achieved by incorporation of small amounts (0.5 to 1.5 percent on dry soil) of P_2O_5 and of fatty amines (0.1 to 0.3 percent on dry soil) with asphalt cutback into very fine-grained soils which could not be stabilized with asphalt alone. Coarser-grained soils, which did develop some wet-stability with asphalt alone, were improved by addition of these additives to a degree far greater than that attainable with asphalt alone at any concentration level. While P_2O_5 had a more pronounced beneficial effect than the amines, combinations of the two compounds, added to very plastic soils, produced much greater stability than either compound alone with asphalt. Finer soils, in general, required higher concentrations of asphalt and additives for satisfactory stabilization than coarser ones.

2. Molding water content was found to be an important variable affecting strength and water resistance; stability was maximum at or slightly below optimum water content for compaction, and decreased rapidly at higher levels. Additives such as P_2O_5 and amines, however, rendered successful stabilization possible over a much broader water-content range than attainable with asphalt alone.

3. Asphalts derived from various crudes, and of varying hardness, while varying appreciably in their soil stabilizing ability when used alone, all showed marked enhancement in stabilizing ability on incorporation of P_2O_5 and/or amines. Anomalously, harder asphalts were found to be better soil stabilizers (either alone or with additives) than softer asphalts.

4. Asphalt cutbacks prepared with highly volatile solvents (for example, hexane, gasoline) were found, contrary to general belief, to be significantly better stabilizers than medium-curing (for example, kerosene) cutbacks, and also to respond more dramatically to chemical additives. Similarly, low-solvent-content cutbacks were

found to be superior to cutbacks of high solvent content.

5. A wide variety of acidic phosphorus-bearing compounds, when added in low concentrations to cutback-treated soils, were found to be even more effective stabilization aids than P_2O_5 . Greatest improvements were observed with benzene phosphonic acid; most interesting from the economic standpoint was 85 percent phosphoric acid, which is considerably less costly than P_2O_5 . Other organic and mineral acids (notably, hydrochloric acid) were found to be promising stabilizing-aids, although generally less effective than the phosphorus compounds.

From the results of this investigation, a theory of the mechanism of asphalt-stabilization of soils, and of additive-action, has been developed; this theory may be helpful in guiding further research in this area. From the practical standpoint, it has been concluded that the use of small amounts of appropriate chemical additives may make economically practicable the successful stabilization, with asphalt, of a broad spectrum of fine-grained, high-plasticity soils whose stabilization by conventional techniques would be either costly or impossible. Field-evaluation of these stabilizing systems is strongly recommended.

● **ALTHOUGH** asphalt and related bituminous materials have been found generally to be of limited utility as stabilizers for fine-grained soils, it has for some time been postulated that the incorporation of small quantities of selected chemicals with asphalt in soils would result in significant improvements in soil stability. In an earlier study (1), the authors undertook research to confirm this postulation, and were able to demonstrate that the strength and resistance to moisture-attack of an asphalt-cutback-treated clayey silt could indeed be greatly improved by the incorporation of small quantities (0.2 to 0.5 percent on the soil) of selected fatty amines, phosphorus pentoxide, and certain other compounds. Analysis of the results of this study led to the deduction that at least one function of these additives was to enhance the adhesion of asphalt to soil under wet conditions, with consequent improvement in asphalt-distribution and in blockage of water-uptake by the soil on immersion. The results of this earlier study were sufficiently promising to warrant a more extensive investigation, aimed at answering the following questions:

1. Are the observed effects produced by amines and phosphorus pentoxide manifested with a variety of different soils, and of different asphalts?
2. Can these two types of additive be employed together, in conjunction with asphalt, to yield still further improvements in soil stability?
3. Do there exist compounds of reactivity comparable with phosphorus pentoxide, which are yet more effective in asphalt stabilization?
4. By what mechanism or mechanisms does P_2O_5 improve the stabilizing ability of asphalt?

Satisfactory resolution of these questions constituted the objective of the studies herein described. For the sake of clarity, the work is described in four major sections, each of which can be considered independently of the others. These are:

- A. Fatty Amines and Phosphorus Pentoxide as Additives to Asphalt-Cutback-Stabilized Soils: Effect of Soil Type.
- B. Fatty Amines and Phosphorus Pentoxide as Additives to Asphalt-Cutback-Stabilized Soils: Effect of Curing Conditions and Molding Water Content.
- C. Fatty Amines and Phosphorus Pentoxide as Additives to Asphalt-Cutback-Stabilized Soils: Effect of Variations of Asphalt and Cutback Composition.
- D. Other Reactive Chemical Additives as Aids to Cutback Stabilization.

An effort is made to bring the diverse results into proper relation and perspective and a series of hypotheses and general conclusions are presented.

A. FATTY AMINES AND PHOSPHORUS PENTOXIDE AS ADDITIVES TO ASPHALT-CUTBACK STABILIZED SOILS: EFFECT OF SOIL TYPE.

Materials and Procedure

Five soils of widely differing engineering properties were examined in this study; the important distinguishing characteristics of these soils are shown in Table 1. All the soils were air-dried and screened through a No. 10 sieve. Repeated ball-milling was employed to crush large aggregates of soil. The fraction of soil retained by this sieve, consisting mainly of stones, was then discarded.

Straight run, steam and vacuum refined asphalt manufactured by Shell Oil Co. (Code No. HOA-2635, of 40-50 penetration) was used for asphalt-gasoline cutback preparation. Two parts (by weight) of asphalt were shaken with one part of unleaded gasoline until the mixture appeared to be completely uniform.

A Brabender Plastograph equipped with a finger-prong mixer and automatic mixing torque recorder was used as mixing apparatus in most of the experiments. A two stage mixing procedure was employed. The first step consisted of premixing of soil and water, or soil, water and additive if the additive was soluble in water. Generally, a three minute mixing period was sufficient to reach equilibrium mixing torque, which indicated uniform water distribution throughout the soil. The second step was mixing of soil-water mixture with stabilizer: asphalt cutback, or asphalt cutback treated with P_2O_5 . (Incorporation of P_2O_5 into asphalt cutback was achieved simply by blending the two ingredients with a spatula just before addition of stabilizer to the soil-water mixture.) The addition of stabilizer to the soil-water mixture was carried out in the same manner in all experiments. The weighed quantity of stabilizer was poured into a groove cut in the middle of the mixture between the two parallel rotating mixer shafts. The mixer was kept covered, when possible, to minimize evaporation of volatile

TABLE 1
SUMMARY OF PHYSICAL AND CHEMICAL PROPERTIES AND MINERALOGICAL COMPOSITION
OF SOILS USED IN STABILIZATION INVESTIGATIONS

		Portsmouth Silty Sand (PSS)	Massachusetts Clayey Silt (M-21)	Fort Belvoir Sandy Clay (FBSC)	Vicksburg Loess (VL)	Vicksburg Buckshot Clay (VBC)
Engineering Properties	Specific gravity	2.69	2.77	2.72	2.80	2.87
	Liquid limit (%)	-	20.0	32.0	40.8	60.0
	Plastic limit (%)	-	14.0	18.0	26.0	27.8
	Plasticity index (%)	-	6.0	14.0	14.8	32.2
	Optimum water content (%)	14.2	12.3	16.5	18.2	22.0
	Max. as-molded density, lbs. dry soil/ft ³	115.0	121	110.0	105.0	105.0
Chemical Properties (74 μ fraction)	Cat. Ex. Cap. (m. e./100gm.)	2.0			16.0	30
	pH	4.8			4.6	4.6
	Soluble salts (%)	0.3			0.2	0.3
	Fe ₂ O ₃	1.5 \pm 0.1	2.9	-	1.6 \pm 0.1	1.9 \pm 0.1
	Organic Matter	0.9 \pm 0.1			1.8 \pm 0.1	1.1 \pm 0.1
	Ethylene glycol retention (mg./gm.)	14	21	26	32	65
Mineralogical Composition (74 μ fraction) (Determined by DTA, X-ray, and Microscopy)	Quartz	35 \pm 3	35	40	30 \pm 3	20 \pm 3
	Feldspar	50 \pm 10	20		20 \pm 10	20 \pm 10
	Kaolinite	-	-	25	-	-
	Illite	10 \pm 15	30	-	15 \pm 3	25 \pm 3
	Chlorite	3 \pm 2	-	-	-	-
	Montmorillonoid	-	-	-	20 \pm 3	25 \pm 3
Particle Size (Sedimen- tation)	% Finer than 1 mm	85	295	100	100	100
	" " "0.1 mm	47	62	61	100	100
	" " "0.01 mm	12	22	28	28	55
	" " "0.002 mm	3	10	18	3	35
Typical Strength Data	Dry Density, lb/ft ³	116	123	118	108	123
	Dry compressive strength, psi	80 \pm 5	340 \pm 10	180 \pm 3	440 \pm 10	790 \pm 40
	% volumetric shrinkage on drying	0.9	0.8	5.1	2.8	14.6

ingredients. In order to standardize mixing throughout the experiments, two minutes' mixing time was selected. Previous investigations of mixing time effect on properties of asphalt-stabilized soil had indicated that mixing for two minutes resulted in a homogeneous mixture, and further mixing did not appreciably change the strength characteristics of stabilized soil samples.

After mixing, the soil mixture was statically compacted into a Harvard Miniature Compaction mold to a density approximately equal to that achieved by standard dynamic compaction (effort approximately standard AASHTO) of the same mixture. Six test-samples were made of each composition, each sample being weighed, and its volume determined by mercury displacement, immediately after molding.

In order to reduce the effect of daily variations in ambient relative humidities and temperatures, all six cylindrical test samples were placed for curing in open desiccators over saturated aqueous potassium carbonate solution, which provided a constant relative humidity of approximately 43 percent. Weight loss and changes in volume by mercury displacement method were recorded periodically throughout the curing period of fourteen days. Three samples were tested in the laboratory testing machine for as cured unconfined compressive strength. The remaining three samples were immersed in water for a period of seven days, and after recording the changes in weights and volumes, were tested for unconfined compressive strength. In all cases, the residual volatiles content at testing was determined by drying the broken samples in an oven at 100 C for 24 hours.

Results

Table 2 shows the unconfined compressive strengths of air dried, unstabilized samples of all soils compacted at optimum water contents for maximum density; and shrinkage characteristics of these soils upon drying.

Tables 3 to 7 present in summarized form the complete results of the effects of antistripping additives and phosphorus pentoxide on the five cutback-stabilized soils used in this study. Two asphalt concentrations (5 and 10 percent based on the weight of dry soil) were used on each soil, although the results indicate that the use of 10 percent of asphalt on coarser soils (Portsmouth sandy silt) is excessive, and 5 percent of asphalt on finer soils (Vicksburg Buckshot) is insufficient.

Two amines, Armeen 12D and Armeen 18D acetate, at different concentrations (0.1 to 0.3 percent on soil), and phosphorus pentoxide at two concentrations (10 and 30 percent based on asphalt) were investigated.

Since the unconfined compressive strength of immersed samples is considered to be a significant criterion for stabilization of soils, the effects of various additives on this property are illustrated graphically in Figures 1 and 2. Because equivalent results were obtained with both amine additives, the effects of only Armeen 12D are included in these figures. Due to the use of a new batch of Massachusetts clayey silt (M-21), the data presented in this report do not coincide with results reported previously on this soil (1). The proportional improvements produced by additives, are, however, in reasonable agreement with the earlier data.

TABLE 2

COMPRESSIVE STRENGTHS OF AIR-DRIED, UNTREATED SOIL SAMPLES

Soil	At Molding		14 Days' Air Drying			Volumetric Shrinkage-percent of molded volume
	Water Content percent	Dry Density lb/ft ³	Water Content percent	Dry Density lb/ft ³	Compressive Strength psi	
Portsmouth Silt	13.8	113	1.4	114	81 ⁺⁵	1.5
Mass. Clayey Silt (M-21)	11.5	121	1.0	122	342 ⁺¹²	1.7
Ft. Belvoir Sandy Clay	17.2	112	2.2	118	180 ⁺³	5.8
Vicksburg Loess	18.1	105	1.7	108	440 ⁺¹⁰	3.6
Vicksburg Buckshot	21.0	105	4.8	123	785 ⁺⁴⁰	14.5

Note: All numbers in the Table are averages of three samples.

TABLE 3

EFFECT OF PHOSPHORUS PENTOXIDE AND ANTISTRIPPING ADDITIVES ON PORTSMOUTH SANDY SILT STABILIZED WITH ASPHALT CUTBACK

Mixing Water Content - 14.2%; Asphalt Cutback Composition - 2:1 Asphalt to Gasoline

Asphalt Concentration - 1% ¹ ; Aggregate Subgrade Composition - 1% ¹ Aggregate to Subgrade												
At Molding				14 Days Cure			7 Days Water Immersion					
Asphalt Concentration % on Soil	Additive ¹ and Concentration %	Volatiles Content %	Density lb/ft ³	Volatiles Content %	Density lb/ft ³	Compressive Strength psi	Volatiles Content %	Water Absorption %	Density lb/ft ³	Compressive Strength psi	Ratio: Rewet C. S. Cured C. S.	
5	None	13.6	113	0.8	116	238 ⁺⁹	6.1	5.3 ^{+0.1}	115	78 ⁺³	0.33	
5	P ₂ O ₅ - 0.5	13.8	112	0.7	116	227 ⁺¹⁶	6.8	5.6 ^{+0.2}	116	98.5 ⁺¹¹	0.43	
5	P ₂ O ₅ - 1.5	13.8	112	1.2	116	252 ⁺³⁵	5.7	4.4 ^{+0.2}	117	125 ⁺²	0.51	
5	A12D - 0.1	13.8	112	1.0	114	158 ⁺¹⁵	4.9	4.0 ^{+0.1}	114	75 ⁺⁵	0.48	
5	A18DA - 0.1	13.6	113	0.6	116	203 ⁺⁹	6.2	5.3 ^{+0.2}	115	86.5 ⁺²	0.42	
5	A12D - 0.1	13.8	114	0.7	116	198 ⁻¹	4.5	3.4 ^{+0.1}	116	116 ⁻³	0.59	
	P ₂ O ₅ - 0.5											
10	None	14.4	106	0.7	110	195 ⁺²¹	4.7	4.0 ^{+0.4}	109	101 ⁺⁹	0.52	
10	P ₂ O ₅ - 1.0	14.7	106	1.2	110	218 ⁺²⁵	4.0	2.6 ^{+0.2}	109	149 ⁺⁷	0.70	
10	P ₂ O ₅ - 3.0	15.2	-	2.2	111	332 ⁺²⁰	6.7	4.2 ^{+0.1}	110	117 ⁺¹⁵	0.53	
10	A12D - 0.1	14.5	-	0.5	110	93 ⁻⁰	6.4	5.9 ^{+0.2}	109	76 ⁺⁵	0.82	
10	A12D - 0.1	14.5	-	1.0	111	182 ⁻³	4.7	3.7 ^{+0.1}	109	122 ⁻⁵	0.67	
	P ₂ O ₅ - 1.0											
10	A12D - 0.3	14.5	107	1.7	111	216 ⁺¹⁵	5.2	3.8 ^{+0.3}	110	155 ⁺⁶	0.72	
	P ₂ O ₅ - 3.0											

¹ A12D = Armeen 12D (lauryl amine)

A18DA = Armeen 18D Acetate (octadecyl amine acetate)

P₂O₅ = Phosphorus Pentoxide

All concentrations of additives are based on dry weight of soil.

All numbers in the table are averages of three samples.

TABLE 4

EFFECT OF PHOSPHORUS PENTOXIDE AND ANTISTRIPPING ADDITIVES ON MASSACHUSETTS CLAYEY SILT (M-21) STABILIZED WITH ASPHALT CUTBACK

Mixing Water Content - 11.0%; Asphalt Cutback Composition - 2:1 Asphalt to Gasoline

At Molding		14 Days Cure				7 Days Water Immersion					Ratio:
Asphalt Concentration % on Soil	Additive ¹ and Concentration %	Volatiles Content %	Density lb/ft ³	Volatiles Content %	Density lb/ft ³	Compressive Strength psi	Volatiles Content %	Water Absorption %	Density lb/ft ³	Compressive Strength psi	Rewet C. S. Cured C. S.
5	None	11.0	120	1.4	122	440 ⁺²	7.1	6.3 ^{+0.2}	117	57 ⁺⁶	0.13
5	P ₂ O ₅ - 0.5	10.8	119	0.9	122	408 ⁺¹⁷	6.9	5.5 ^{+0.4}	121	96 ⁺⁷	0.24
5	P ₂ O ₅ - 1.5	10.7	119	1.2	121	409 ⁺²⁰	6.8	4.9 ^{+0.1}	118	110 ⁺⁶	0.27
5	A12D - 0.1	10.7	119	1.0	121	382 ⁺¹⁶	7.9	7.1 ^{+0.1}	118	46 ⁺⁴	0.11
5	A18DA - 0.1	10.8	-	0.8	122	391 ⁺⁴	7.7	6.8 ^{+0.4}	120	69 ⁺⁷	0.18
5	{ A12D - 0.1 P ₂ O ₅ - 0.5	10.8	118	0.9	119	255 ⁻¹⁵	7.3	6.2 ^{-0.1}	118	82 ⁻¹²	0.28
5	{ A18DA - 0.1 P ₂ O ₅ - 0.5	11.0	-	0.8	121	351 ⁻¹³	7.8	6.8 ^{+0.2}	119	74 ⁺⁵	0.21
5	{ A12D - 0.3 P ₂ O ₅ - 1.5	10.8	118	1.3	121	431 ⁺²²	4.2	2.6 ^{+0.1}	120	208 ⁺¹⁷	0.48
10	None	11.2	113	0.6	116	353 ⁺⁵	4.1	3.2 ^{+0.3}	113	122 ⁺¹²	0.34
10	P ₂ O ₅ - 1.0	11.3	115	1.1	120	405 ⁺⁰	3.7	2.3 ^{+0.1}	118	269 ⁺¹⁰	0.67
10	P ₂ O ₅ - 1.5	11.3	114	1.2	119	433 ⁺¹⁰	3.2	1.9 ^{+0.1}	118	325 ⁺⁷	0.75
10	P ₂ O ₅ - 3.0	11.0	114	2.0	118	440 ⁺²⁴	3.6	1.6 ^{+0.1}	117	305 ⁺⁵	0.70
10	A12D - 0.3	10.9	114	1.0	118	290 ⁺¹⁰	3.9	2.9 ^{+0.1}	116	142 ⁺⁹	0.49
10	{ A12D - 0.3 P ₂ O ₅ - 3.0	10.9	116	1.6	121	382 ⁻¹⁰	3.7	2.0 ^{-0.2}	119	315 ⁺¹⁰	0.82

¹ A12D = Armeen 12D (lauryl amine)

A18DA = Armeen 18D Acetate (octadecyl amine acetate)

P₂O₅ = Phosphorus Pentoxide

The concentrations of additives are based on dry weight of soil. Soil shipment of December, 1955.

All numbers in Table are averages of three samples.

Table 8 and Figure 3 shows the effect of 3 percent of phosphorus pentoxide (P₂O₅) without asphalt on the properties of different soils. These tests were made in order to compare the stabilizing effect of P₂O₅ alone with the results when P₂O₅ and asphalt are used together.

Discussions of the Results

Characteristics of Unstabilized Samples. As it is seen from the Table 2, the compressive strengths of air-dry, unstabilized samples of various soils correlate with the grain size distribution of the soils in such a manner that finer grained soils, possessing higher specific surface, exhibit higher strengths. (None of these soils,

incidentally, retain any significant strength on water-immersion.) Fort Belvoir sandy clay does not fit into this pattern; despite having a higher specific surface than M-21 soil, it shows lower dry compressive strength than the latter soil. Two possible explanations for this anomaly are (a) the clay-mineral component of this soil is kaolinite, while the other soils studied contain the more cohesive illitic or montmorillonoid clay minerals, or (b) the clay mineral component may exist in an aggregated and cemented form due to the presence of a significant quantity of ferric oxide in the soil. Neither of these compositional characteristics are likely to be detected by an ordinary grain-size analysis or by glycol-retention measurements.

It will be noted (Table 2) that specific surface, besides influencing dry compressive strength, also influences shrinkage on drying. More plastic soils, characterized by

TABLE 5

EFFECT OF PHOSPHORUS PENTOXIDE AND ANTISTRIPPING ADDITIVES ON FORT BELVOIR SANDY CLAY STABILIZED WITH ASPHALT CUTBACK

Mixing Water Content - 16%, Asphalt Cutback Composition - 2:1 Asphalt to Gasoline											
At Molding		14 Days Cure				7 Days Water Immersion					Ratio: Rewet C. S. Cured C. S.
Asphalt Concentration % on Soil	Additive ¹ and Concentration %	Volatiles Content %	Density lb/ft ³	Volatiles Content %	Density lb/ft ³	Compressive Strength psi	Volatiles Content %	Water Absorption %	Density lb/ft ³	Compressive Strength psi	
5	None	17.3	106	1.2	111	334 \pm 6	12.5	11.3 \pm 0.1	101	23 \pm 2	0.07
5	P ₂ O ₅ - 0.5	15.9	109	1.1	116	348 \pm 12	13.2	11.9 \pm 0.3	105	28 \pm 2	0.08
5	A12D - 0.2	15.6	107	1.1	113	285 \pm 15	11.3	10.3 \pm 0.1	108	48 \pm 2	0.17
5	A18DA - 0.1	17.9	106	1.6	112	234 \pm 10	11.1	9.7 \pm 0.1	107	40 \pm 5	0.17
5	A12D - 0.2	15.4	107	0.9	112	220 \pm 5	12.4	11.2 \pm 0.3	107	25 \pm 1	0.11
	P ₂ O ₅ - 0.5										
10	None	10.1	99	1.5	103	301 \pm 20	10.9	9.5 \pm 0.3	97	31 \pm 1	0.10
10	P ₂ O ₅ - 1.0	19.5	95	1.9	109	400 \pm 22	8.7	7.2 \pm 0.5	105	132 \pm 0	0.32
10	P ₂ O ₅ - 3.0	16.6	98	2.2	110	483 \pm 18	8.5	5.4 \pm 0.1	104	205 \pm 5	0.42
10	A12D - 0.3	17.1	98	1.1	104	327 \pm 10	8.3	5.2 \pm 0.1	107	214 \pm 20	0.48
	P ₂ O ₅ - 3.0										

¹ A12D = Armeen 12D (lauryl amine)

A18DA = Armeen 18D Acetate (octadecyl amine acetate)

P₂O₅ = Phosphorus Pentoxide

All numbers in the Table are averages of three samples. The concentrations of additives are based on dry weight of soil.

TABLE 6

EFFECT OF PHOSPHORUS PENTOXIDE AND ANTISTRIPPING ADDITIVES ON VICKSBURG LOESS STABILIZED WITH ASPHALT CUTBACK

Mixing Water Content - 18.2%; Asphalt Cutback Composition - 2:1 Asphalt to Gasoline											
At Molding		14 Days Cure				7 Days Water Immersion					Ratio: Rewet C. S. Cured C. S.
Asphalt Concentration % on Soil	Additive ¹ and Concentration %	Volatiles Content %	Density lb/ft ³	Volatiles Content %	Density lb/ft ³	Compressive Strength psi	Volatiles Content %	Water Absorption %	Density lb/ft ³	Compressive Strength psi	
5	None	18.3	104	1.9	109	517 \pm 21	18.2	16.0 \pm 0.2	100	14 \pm 0	0.03
5	P ₂ O ₅ - 0.5	18.8	104	2.2	109	517 \pm 18	16.7	14.2 \pm 0.1	101	22 \pm 1	0.04
5	A12D - 0.1	18.3	105	1.4	110	610 \pm 37	19.4	18.0 \pm 0.1	100	18 \pm 2	0.03
5	A18DA - 0.1	18.2	104	1.3	109	502 \pm 17	17.7	16.0 \pm 0.1	101	21 \pm 3	0.04
5	A12D - 0.1	18.4	106	1.6	110	592 \pm 60	17.7	15.9 \pm 0.3	101	32 \pm 3	0.06
	P ₂ O ₅ - 0.5										
5	A18DA - 0.1	17.9	106	1.3	111	566 \pm 53	18.2	16.6 \pm 0.5	102	30 \pm 5	0.05
	P ₂ O ₅ - 0.5										
10	None	18.7	99	1.4	104	396 \pm 32	12.4	11.0 \pm 0.3	94	26 \pm 1	0.07
10	P ₂ O ₅ - 1.0	18.2	99	1.5	105	367 \pm 35	9.6	7.7 \pm 0.2	100	68 \pm 5	0.19
10	P ₂ O ₅ - 3.0	17.4	103	2.1	107	452 \pm 23	6.8	4.6 \pm 0.2	104	140 \pm 6	0.31
10	A12D - 0.1	18.9	98	1.2	103	401 \pm 21	13.1	11.8 \pm 0.1	96	25 \pm 6	0.06
10	A12D - 0.3	17.1	100	1.1	105	495 \pm 30	8.1	7.0 \pm 0.1	102	77 \pm 6	0.16
10	A18DA - 0.2	18.4	98	1.3	103	413 \pm 37	13.8	12.9 \pm 0.1	98	33 \pm 2	0.08
10	A12D - 0.2	17.3	101	1.1	106	355 \pm 12	9.8	8.2 \pm 0.4	101	81 \pm 5	0.23
	P ₂ O ₅ - 1.0										
10	A18DA - 0.2	18.2	100	1.4	105	485 \pm 25	12.2	10.3 \pm 0.6	102	63 \pm 11	0.13
	P ₂ O ₅ - 1.0										
10	A12D - 0.3	17.9	103	2.2	107	560 \pm 14	5.8	3.7 \pm 0.2	107	287 \pm 4	0.51
	P ₂ O ₅ - 3.0										

¹ A12D = Armeen 12D (lauryl amine)

A18DA = Armeen 18D Acetate (octadecyl amine acetate)

P₂O₅ = Phosphorus Pentoxide

The concentrations of additives are based on dry weight of soil.

All numbers in the Table are averages of three samples.

larger specific surface, shrink more upon drying than soils of lower plasticity. Here, again, one soil—Vicksburg loess—appears to be an exception; the rather narrow particle-size distribution of this soil, and the absence of a very fine size-fraction, may explain this anomaly.

Characteristics of Unmodified Cutback-Stabilized Samples. The physical characteristics of various soils stabilized with 5 and 10 percent asphalt in asphalt cutback form are presented in Tables 3 to 7, and Figures 1 and 2. Effective stabilization of soils of high plasticity with 5 percent asphalt was not possible. Therefore, the effects of higher asphalt concentration (10 percent) were studied and the results are shown in these tables.

One immediate general observation can be made from these results: soils composed of finer particles and thus possessing greater specific surface area are more difficult to stabilize with asphalt cutbacks than coarser soils. Greater amounts of asphalt are required with these soils to produce samples of reasonable stability against water action. Upon water immersion, fine-grained soils stabilized with asphalt cutbacks absorb larger amounts of water, undergo greater swelling, and show lower rewet compressive strengths than coarser soils.

Two factors can be considered in explaining this behavior. First, due to the high specific surface of the finer soils, the asphalt is too thinly distributed to be entirely effective against water penetration. Second, due to the high adsorptive affinity of fine-grained soils for water, firm adhesion between the asphalt and the soil particle surfaces probably does not develop during the curing period. In both instances, water

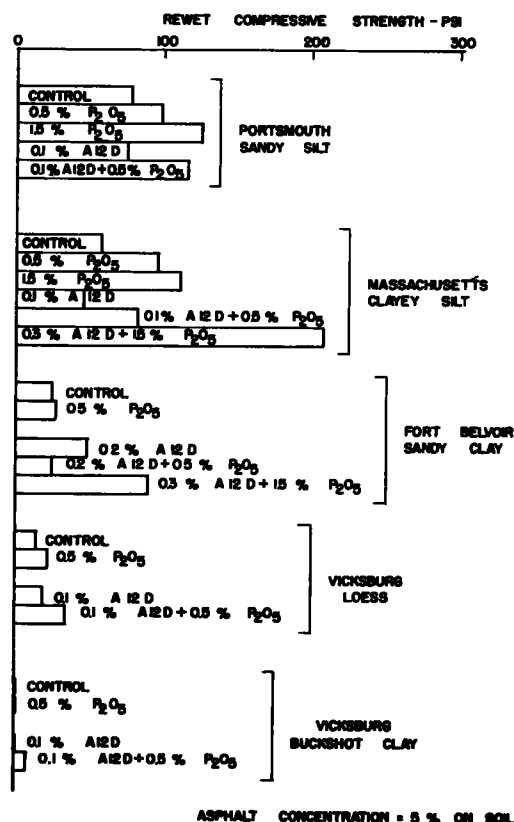


Figure 1. Effect of phosphorus pentoxide and antistripping additives on rewet compressive strength of various soils.

TABLE 7

EFFECT OF PHOSPHORUS PENTOXIDE AND ANTISTRIPPING ADDITIVES ON VICKSBURG BUCKSHOT STABILIZED WITH ASPHALT CUTBACK

Mixing Water Content - 22.7%; Asphalt Cutback Composition - 2:1 Asphalt to Gasoline

Asphalt Concentration % on Soil	Additive ¹ Concentration %	At Molding		14 Days Cure		7 Days Water Immersion				Ratio: Rewet C. S. Cured C. S.
		Volatiles Content %	Density lb/ft ³	Volatiles Content %	Density lb/ft ³	Compressive Strength psi	Volatiles Content %	Water Absorption %	Density lb/ft ³	Compressive Strength psi
5	None	21.8	99	4.1	117	648 ± 133	Samples Disintegrated			
5	P ₂ O ₅ -0.5	21.2	101	4.4	119	710 ± 220				
5	A12D-0.1	19.0	101	2.8	115	714 ± 51	22.7	18.6 ± 0.3	99	7 ± 2
10	None	20.8	94	3.0	107	502 ± 64	Samples Disintegrated			
10	P ₂ O ₅ -1.0	20.8	96	3.6	107	526 ± 48				
10	P ₂ O ₅ -3.0	18.1	101	4.2	109	366 ± 18	15.7	11.5 ± 0.4	98	59 ± 7
10	A12D-0.2	20.7	95	3.4	105	548 ± 8	23.0	19.8 ± 1.2	95	14 ± 4
10	A12D-0.2	20.0	99	3.7	111	625 ± 30	16.3	13.5 ± 2.0	-	42 ± 6
10	P ₂ O ₅ -1.0	18.6	99	4.2	108	406	13.7	8.4 ± 0.5	100	125 ± 12
10	A12D-0.3									
10	P ₂ O ₅ -3.0									

¹ A12D = Armeen 12D (lauryl amine)

P₂O₅ = Phosphorus Pentoxide

All numbers in the Table are averages of three samples. The concentrations of additives are based on dry weight of soil.

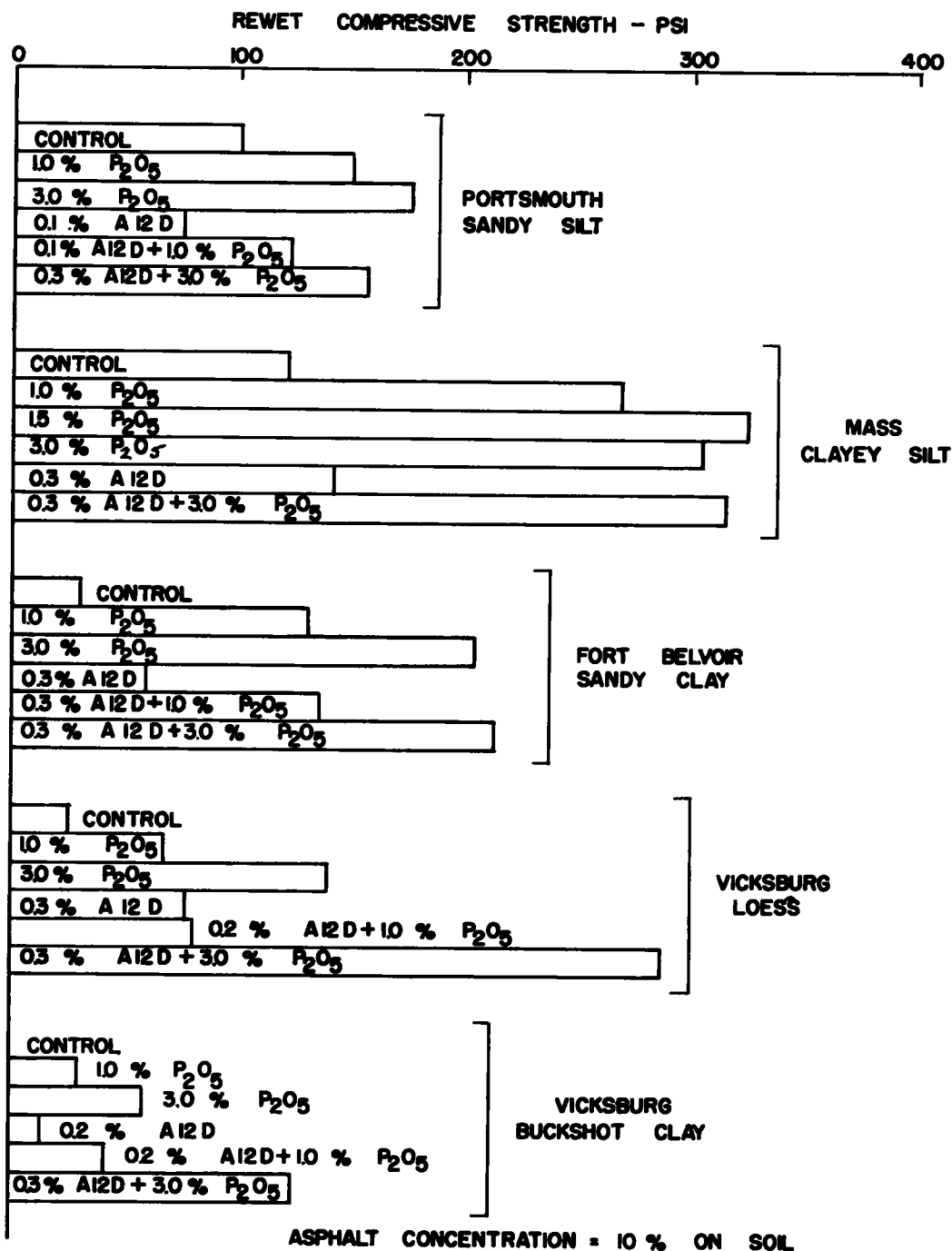


Figure 2. Effect of phosphorus pentoxide and antistripping additives on rewet compressive strength of various soils.

picked up by the asphalt-treated sample will tend to migrate into the soil-asphalt or soil-soil interfaces, weakening or destroying the adhesive or cohesive bonds holding the particles together.

The degree of distribution of asphalt throughout a soil mass is a critical factor in stabilizing the soils. Although no specific study was made of the effect of mixing in this work, all soils were mixed until the samples visually appeared to be uniform. Finer-grained soils required longer mixing times to produce samples of uniform appearance.

TABLE 8
EFFECT OF PHYSICAL PROPERTIES OF VARIOUS SOILS TREATED WITH PHOSPHORUS PENTOXIDE
Phosphorus Pentoxide Concentration = 3% on Dry Soil

Name of Soil	At Molding		14 Days Cure			7 Days Water Immersion				Ratio: Rewet C. S. Cured C. S.
	Water Content %	Density lb/ft ³	Water Content %	Density lb/ft ³	Compressive Strength psi	Water Content %	Water Absorption %	Density lb/ft ³	Compressive Strength psi	
Portsmouth Sandy Silt	10.4	127	2.1	132	990 ± 90	9.7	7.4 ± 0.2	130	282 ± 11	0.28
Massachusetts Clayey Silt	11.1	130	2.2	135	1165 ± 130	10.9	8.3 ± 0.2	130	153 ± 13	0.13
Fort Belvoir Sandy Clay	14.6	117	2.4	130	950 ± 50	13.4	10.3 ± 0.3	121	71 ± 6	0.08
Vicksburg Loess	16.6	115	3.1	119	880 ± 80	22.7	18.8 ± 0.4	106	10 ± 2	0.01
Vicksburg Buckshot Clay	18.9	109	5.1	127	1225 ± 100	Samples Disintegrated				

All numbers in the Table are averages of three samples.

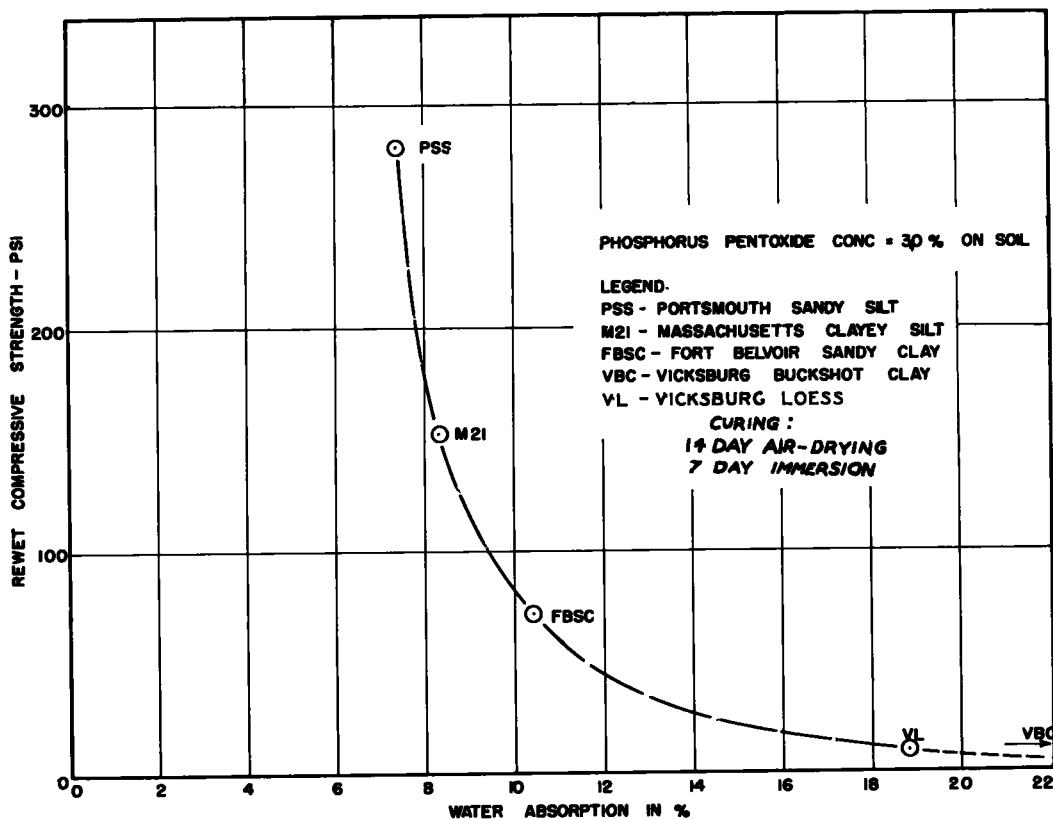


Figure 3. Effect of phosphorus pentoxide on rewet compressive strength of various soils.

Effect of Phosphorus Pentoxide (P_2O_5) on Soils Stabilized with Asphalt Cutback.

The beneficial effects of P_2O_5 at varying concentration on properties of various soils stabilized with asphalt cutbacks (5 or 10 percent of asphalt on dry soil) are shown in Tables 3 to 7, and Figures 1 and 2.

It is interesting to note that rewet compressive strengths of cutback stabilized soils deficient in $< 2 \mu$ fraction (Portsmouth silt, Vicksburg loess) are not increased to the same degree by the presence of P_2O_5 , as are soils of higher clay content. Similarly, P_2O_5 appears to increase the shrinkage on curing of the higher clay content soils (compare density at molding, and after 14 days cure in the tables). On the other hand, all soil samples treated with P_2O_5 exhibit less reswelling upon immersion in water than untreated samples, in spite of the fact that in some cases they absorb more water. These factors suggest that mainly the fine fraction of the soil reacts with P_2O_5 .

Generally, improvements caused by P_2O_5 are dependent on particle surface area of the soil. Although rewet compressive strengths of highly plastic soils are lower than those of non-plastic soils, the percentage improvements relative to control samples are greater with highly plastic soils provided that a sufficient amount of P_2O_5 is used. On the other hand, asphalt content is another factor influencing the effectiveness of P_2O_5 . The strengths of samples stabilized with 10 percent of asphalt are considerably greater than the strengths of samples stabilized with 5 percent of asphalt in spite of the fact that the concentrations of P_2O_5 on the soil are approximately the same in both cases.

In order to obtain more information on the action of P_2O_5 alone on soils, samples of all five soils were prepared without asphalt, using 3 percent treatment of P_2O_5 and employing preparation and testing procedures essentially equivalent to those employed in cutback work.

The results (Table 8 and Figure 3) indicate that 3 percent P_2O_5 exerts an appreciable stabilizing effect on soils, although this effect is quite different in nature from that of asphalt cutback. High water absorption values of the samples immersed in water indicate that P_2O_5 does not waterproof the soil. On the other hand, the high densities and the hardness of samples indicate that the stabilizing effect is rather due to cementing action. (The use of acidic phosphorus compounds as primary soil-stabilizers has, in fact, been shown (2) to be a potentially important stabilization method.) Apparently the presence of asphalt cutback retards this reaction. The extent of cementing action is lower, but the binding is made more stable (insofar as percent loss in stability on immersion is concerned) by the waterproofing property of the asphalt. In some cases (for example, with Portsmouth sandy silt), however, the rewet compressive strength obtained with P_2O_5 alone is greater than the rewet compressive strength with P_2O_5 and asphalt. From this it would be inferred that, with rather coarse grained soils, interparticle cementation is of greater importance than exclusion of water by waterproofing action. The lack of cohesion in coarse grained soils even in the dry state would appear to support this inference. The effects of three different concentrations (1.0, 1.5, 3.0 percent of P_2O_5 on Massachusetts clayey silt M-21 stabilized with 10 percent asphalt) were investigated and the results are shown in Table 4 and Figure 2. The rewet compressive strength values obtained with 1.5 percent of P_2O_5 treatment are greater than the strengths of the samples with 1.0 percent and 3.0 percent. This observation implies that for a given soil there is a specific concentration of P_2O_5 which is most effective for stabilization of the soil. This optimum concentration apparently increases with increasing specific surface of the soil.

Effect of Amines on Soils Stabilized with Asphalt Cutback. Two amines proven (1) to be effective with Massachusetts clayey silt were investigated for their effects on other soils. Armeen 12D (lauryl amine) was added to the soil with mixing water, and Armeen 18D acetate (octadecyl amine acetate) added with asphalt cutback at varying concentrations. Concentrations of these additives were kept between 0.1 percent and 0.3 percent (based on dry soil) with the finer grained soils being treated with higher concentrations.

The results (Tables 3 to 7, Figures 1 and 2) show that although these additives improve the rewet compressive strengths of the soils stabilized with asphalt cutbacks

considerably less than P_2O_5 , the general trends of these improvements (relative to the control samples) are similar; finer soils are, percentage wise, more improved by the antistripping additives than are the coarse soils. Two mechanisms can be envisioned in explaining the effects of these additives. First, due to adsorption of fatty amine molecules by the active sites of the clay mineral surfaces the affinity of this surface for the asphalt cutback is enhanced. Second, total surface area is reduced due to the strong flocculating action of these additives, and, therefore, less asphalt is needed to adequately waterproof the soil surfaces.

Effect of Combinations of Phosphorus Pentoxide and Antistripping Additives on Soils Stabilized with Asphalt Cutbacks. Only one of the two investigated antistripping additives was used in conjunction with P_2O_5 , namely, Armeen 12D (lauryl amine). In order to be consistent in the experimental procedures throughout this study, the amine was incorporated with the soil in the mixing water, and P_2O_5 , with the asphalt cutback.

Two ratios of P_2O_5 to amine were used, depending on the asphalt concentration: for 10 percent asphalt the ratio was 10:1, while for 5 percent asphalt it was 5:1. Actual concentration combinations (based on dry soil weight) of these additives are tabulated below:

<u>5% Asphalt</u>		<u>10% Asphalt</u>	
<u>Armeen 12D</u>	<u>P_2O_5</u>	<u>Armeen 12D</u>	<u>P_2O_5</u>
0.1%	0.5%	0.1%	1.0%
0.3%	1.5%	0.3%	3.0%

Note in Tables 3 to 7 and Figures 1 and 2 that combining the antistripping additives with P_2O_5 improves the rewet compressive strengths of fine grained soils more markedly than the strengths of coarse soils, provided that the concentrations of asphalt and additives are sufficiently high. In the case of Vicksburg loess and Vicksburg Buckshot clay, soils which are difficult to stabilize, rewet compressive strengths obtained with a 10 percent asphalt and 3 percent P_2O_5 (on soil) system were roughly doubled by addition of 0.3 percent of Armeen 12D.

Another significant observation is that for a given strength, various soils show different water absorption values: water absorption tends to be greater with increasing amount of fines (that is, increasing surface area) in the soil. Considering specific characteristics of the additives employed, this behavior indicates that in stabilizing fine grained soils, the effect of the additives which reduce the specific surface of the soils by cementing the grains together (P_2O_5) is greater than the effects of waterproofing (antistripping) agents.

Conclusions

The results above lead to the following tentative conclusions:

1. Phosphorus pentoxide improves the rewet compressive strengths of all aluminosilicate soils stabilized with asphalt cutbacks. Finer soils require greater amounts of P_2O_5 for effective stabilization.
2. Fine-grained soils respond to combined use of P_2O_5 and antistripping additives more markedly than coarse soils at the same concentrations of asphalt.
3. Sufficient amounts of asphalts are required to protect, against the detrimental action of water, the beneficial changes caused by additives. Finer soils require more asphalt for effective stabilization due to their larger specific surface.

B. FATTY AMINES AND PHOSPHORUS PENTOXIDE AS ADDITIVES TO ASPHALT-CUTBACK STABILIZED SOILS: EFFECT OF CURING CONDITIONS AND MOLDING WATER CONTENT

Materials and Procedure

The materials used were essentially the same as described previously (see A) except that Massachusetts clayey silt (M-21), at its natural moisture content of 9 percent, was used for all tests.

Mixing and molding procedures were as earlier described; however, in order to obtain more uniform density distribution throughout the sample, the soil was compacted into the mold by applying static load to both ends of the sample. (Previously, one end static compaction was used.) This change in compactive method, it is believed, permitted more reproducible and uniform preparation of the samples.

The curing conditions selected for the study were as follows:

- a. No cure (testing for compressive strength determination immediately after compaction).
- b. One day cure at 100 percent relative humidity.
- c. One day cure (as above), and one day immersion in water.
- d. No cure, one day immersion in water.

Two water contents were investigated:

- a. Optimum water content for maximum density (11.0 percent).
- b. Water content 1.3 times optimum (14.3 percent).

The incorporation of chemical additives into the soil was carried out in the following manner: First, the fatty amine (Armeen 12D, dispersed in water) was added to the naturally wet soil, and the resultant mixture was well-mixed. Then the asphalt cutback (containing the P_2O_5) was added, and the mixing continued until a uniform mixture resulted.

To prepare soil samples treated with P_2O_5 alone, dry powdered phosphorus pentoxide was added to and thoroughly mixed with the uniformly wet soil. In order to eliminate variations in compressive strength caused by variations in density of the samples at a given water content, an attempt was made to compact all the samples regardless of chemical additive, to the optimum density of the untreated soil. In the case of the soil treated with P_2O_5 alone (without asphalt) this was difficult to accomplish. Because of radical changes in properties of the soil caused by P_2O_5 treatment, higher densities were required in order to compact uniform samples.

Results and Discussion

The effects of Armeen 12D (lauryl amine), phosphorus pentoxide (P_2O_5) and combinations of these two additives on the properties of Massachusetts clayey silt stabilized with asphalt cutback, and cured at various conditions, are shown in Table 9, and Figure 4. The results lead to the following observations:

- a. Addition of either Armeen 12D, P_2O_5 , or both compounds to cutback-stabilized soil enhances both as-cured and rewet strength. P_2O_5 has a far more beneficial effect than the amine, but when the two compounds are used in combination, the benefits of each are nearly additive.
- b. Cutback-stabilized samples treated only with amine undergo no gain in strength on curing at 100 percent relative humidity for one day. In contrast, samples not containing amine increase in strength slightly during such cure. However, amine-treated samples retain considerably higher strength and absorb less water on immersion than do controls.
- c. Cutback-stabilized samples treated with P_2O_5 alone develop significant strength after only 24 hours of cure at 100 percent relative humidity, showing rather low strength as-molded. Of great importance is the fact that these formulations develop strength on curing under water. Incorporation of P_2O_5 also reduces significantly water absorption on immersion. Strength after 1 day cure at 100 percent relative humidity for these formulations is about the same after subsequent water immersion for one day.
- d. Cutback stabilized samples treated with amine and P_2O_5 absorb on immersion less water than samples treated with either additive alone. The beneficial effects of treatment with both additives appear to be most evident in samples which are immersed in water immediately after compaction.
- e. Raising the molding water content from 11 percent to 14.3 percent results in an across-the-board reduction in strength and increase in water absorption on immersion for cutback-stabilized soils.

TABLE 9

EFFECT OF CURING CONDITIONS ON PROPERTIES OF CHEMICALLY MODIFIED, CUTBACK STABILIZED MASSACHUSETTS CLAYEY SILT (M-21)

Asphalt Concentration = 5% on Dry Soil
Asphalt Cutback Composition = 2:1 Asphalt to Gasoline

Mixing Water Content %	Additive and Concentration %	No Cure			1 Day Cure (100% RH)			1 Day Cure 1 Day Water Imm.			1 Day Water Imm.		
		Density lb/ft ³	Vol-atiles Content %	Com-pressive Strength psi	Density lb/ft ³	Vol-atiles Content %	Com-pressive Strength psi	Density lb/ft ³	Vol-atiles Content %	Com-pressive Strength psi	Density lb/ft ³	Vol-atiles Content %	Com-pressive Strength psi
11.0	None	117.3	11.1	24.0 \pm 1	117.2	10.9	30.0 \pm 4	117.5	13.6	8.0 \pm 0	117.2	14.3	6.0 \pm 1
	A12D-0.2	117.4	11.1	28.0 \pm 1	117.9	10.8	31.0 \pm 2	115.5	13.0	18.0 \pm 1	116.4	13.2	18.0 \pm 1
	P ₂ O ₅ -3.0	117.7	10.7	24.0 \pm 1	118.8	10.6	129.0 \pm 11	117.5	11.4	150.0 \pm 11	116.8	13.4	82.0 \pm 3
	A12D-0.2	116.5	10.8	31.0 \pm 1	117.0	10.7	207.0 \pm 10	116.2	11.1	165.0 \pm 30	116.5	12.4	100.0 \pm 16
	P ₂ O ₅ -3.0												
14.3	None	109.0	14.4	15.0 \pm 0	108.6	13.9	17.0 \pm 0	110.5	16.5	8.0 \pm 1	109.6	18.1	4.0 \pm 0
	A12D-0.2	109.2	13.8	25.0 \pm 3	110.2	13.3	30.0 \pm 2	109.0	15.5	15.0 \pm 0	109.0	15.8	13.0 \pm 0
	P ₂ O ₅ -3.0	109.7	13.8	23.0 \pm 0	110.0	12.9	101.0 \pm 3	113.6	14.5	92.0 \pm 7	113.0	16.5	47.0 \pm 0
	A12D-0.2	111.4	13.9	32.0 \pm 0	110.4	13.4	119.0 \pm 6	111.3	14.9	106.0 \pm 7	112.2	16.3	50.0 \pm 0
	P ₂ O ₅ -3.0												

TABLE 10

EFFECT OF PHOSPHORUS PENTOXIDE ON PROPERTIES OF MASSACHUSETTS CLAYEY SILT UNDER VARIOUS CURING CONDITIONS¹

CRACKS SET UNDER VARIOUS CURING CONDITIONS													
Mixing Water Content %	Additive and Concentration %	No Cure			1 Day Cure (100% RH)			1 Day Cure 1 Day Water Imm.			No Cure 1 Day Water Imm.		
		Density lb/ft ³	Water Content %	Com-pressive Strength psi	Density lb/ft ³	Water Content %	Com-pressive Strength psi	Density lb/ft ³	Water Content %	Com-pressive Strength psi	Density lb/ft ³	Water Content %	Com-pressive Strength psi
11.0	None	113.7	10.9	27 \pm 4	113.1	10.8	29 \pm 3	Samples Disintegrated					
	P ₂ O ₅ -3.0	128.3	10.6	65 \pm 5	128.9	10.3	241 \pm 25	130.5	10.8	335 \pm 3	Samples Disintegrated		
14.3	None	118.9	14.1	18	120.0	14.2	20	Samples Disintegrated					
	P ₂ O ₅ -3.0	121.8	13.7	20	121.7	13.4	165 \pm 20	121.8	13.8	125 \pm 2	121.2	17.4	31 \pm 10

¹ All numbers in the table are the averages of two samples.² Concentration of additive is based on dryweight of soil.

f. Soil treated with P₂O₅ only (Table 10, Figure 5) develops, in 24 hours at 100 percent relative humidity, strength far higher than cutback-stabilized soil containing P₂O₅, and also retains higher strength on immersion in water. However, such formulations disintegrate (or develop little strength) in water immediately after compaction. Compacted densities of P₂O₅-treated soil are far higher than those of cutback-stabilized soil. Increasing the mixing water content has an even more detrimental effect on strength than is observed with cutback systems.

These results indicate strongly that P₂O₅-amine-modified asphalt cutback systems offer considerable promise as fine-grained soil stabilizers, since soils so treated develop suitable strength in one day under wet conditions. While treatment with P₂O₅ alone also results in stabilization, the inability of such formulations to withstand immersion in water immediately after treatment may impose limitations on its use under extreme field conditions.

The mechanism of action of P₂O₅ and amines in soils has been further clarified by this study. It is clear that phosphorus pentoxide functions (both alone, and in conjunction with asphalt) primarily by reacting with the soil minerals and forming an interparticle cement. In addition, it appears that the presence of asphalt to some extent

interferes with the inter-particle cementation process; however, this interference is to a degree compensated for by the apparent ability of P_2O_5 to enhance the coating of soil with asphalt. This is evidenced by the fact that uncured P_2O_5 asphalt stabilized samples, when immersed in water, absorb less water than samples stabilized with

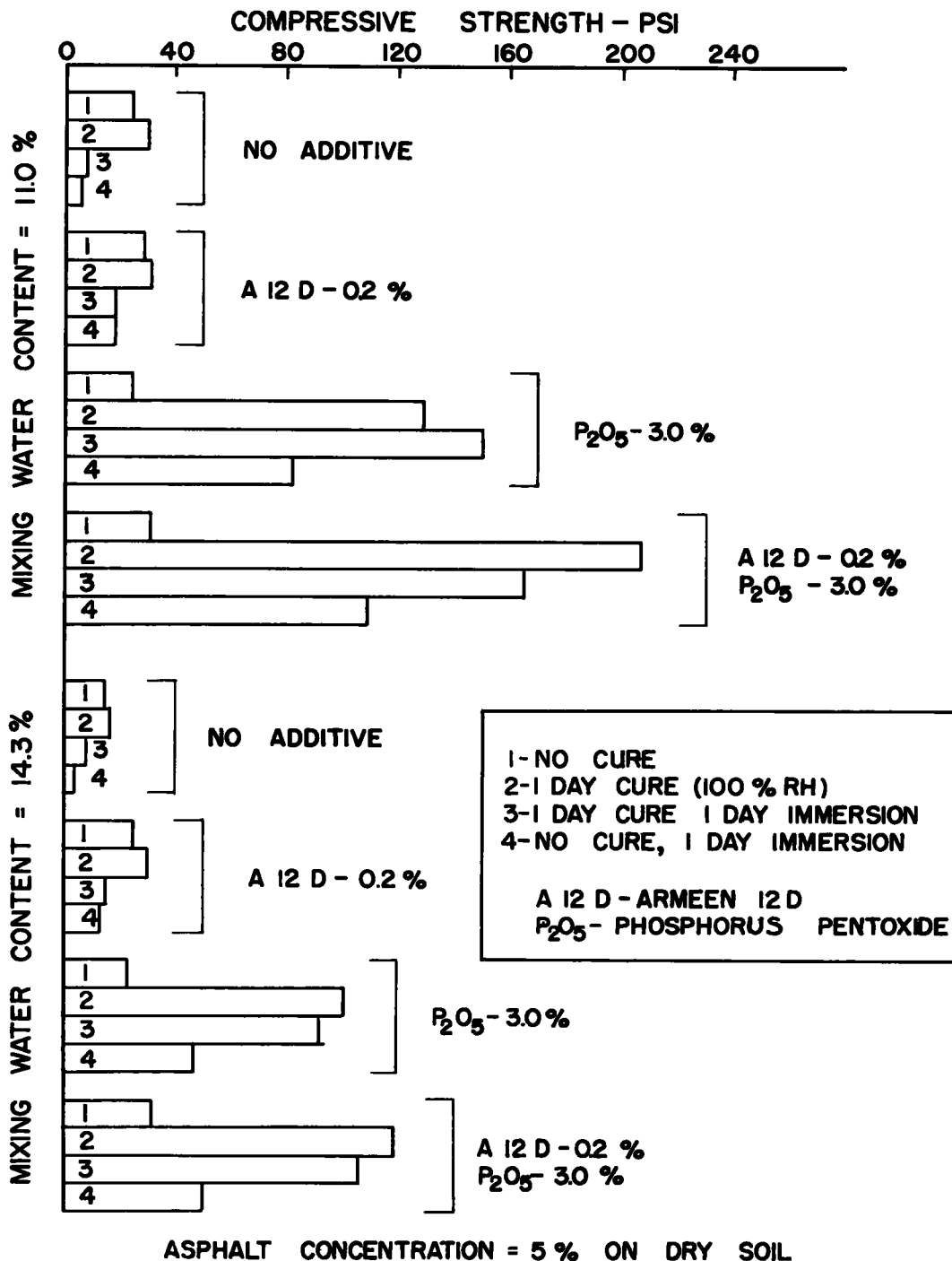


Figure 4. Effect of curing conditions on properties of chemically modified, cutback stabilized Massachusetts clayey silt.

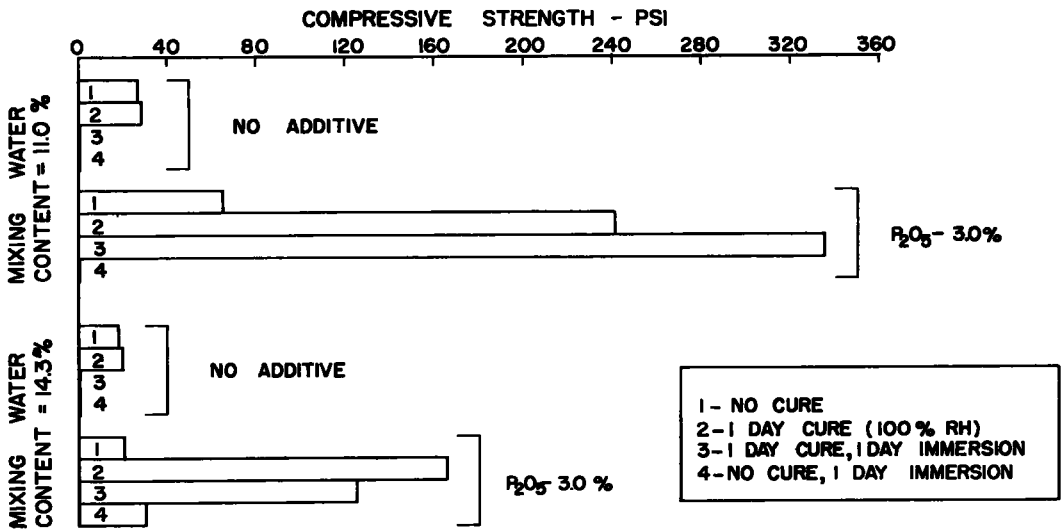


Figure 5. Effect of phosphorus pentoxide on properties of Massachusetts clayey silt cured at different conditions.

asphalt alone. It seems justifiable to postulate, therefore, that (a) the stabilizing action of P_2O_5 is due to cementation, and that this process occurs most satisfactorily in the presence of a limited quantity of water, and (b) the combination of P_2O_5 with asphalt cutback and amine stabilizes soil by both cementation and waterproofing, the latter two components serving to prevent entry of water into soil before the cementation process has taken place.

Conclusions

The results of this study lead to the following conclusions:

- Addition of lauryl amine to cutback-stabilized M-21 soil produces a small improvement in strength which is immediately evident after compaction, and is independent of time of cure under saturated conditions.
- Addition of P_2O_5 to cutback-stabilized M-21 produces no change in strength immediately after compaction, but produces a very large improvement in strength after 24 hours' cure under saturated conditions.
- P_2O_5 -modified, asphalt-stabilized M-21 soil develops high strength when allowed to age for 24 hours totally immersed in water.
- P_2O_5 -and-amine-modified, asphalt-stabilized M-21 soil is superior to that not containing amine, with respect to strength-development under wet conditions.
- M-21 soil treated with P_2O_5 alone will develop high strength after 24 hours at 100 percent relative humidity, but will not develop strength under water.
- M-21 soil treated with P_2O_5 alone, or soil stabilized with asphalt cutback modified with P_2O_5 and/or lauryl amine, develops significantly higher strengths when mixed at optimum water content than at a water content 1.3 times optimum.

C. FATTY AMINES AND PHOSPHORUS PENTOXIDE AS ADDITIVES TO ASPHALT-CUTBACK STABILIZED SOIL: EFFECT OF VARIATIONS IN ASPHALT AND CUTBACK COMPOSITION

Introduction

The greater part of the preceding work was aimed at improving the effectiveness of asphalt as a soil stabilizer by addition of chemical compounds which were expected to influence beneficially the physical characteristics of soil-asphalt systems. To reduce the number of variables, tests were confined to a single (straight-run) asphalt,

and a single cutback solvent at a fixed concentration.

It is well recognized that individual asphalts, even when obtained from the same source and processed in the same manner, vary considerably in their properties as is indicated by simple identification or classification tests such as determination of penetration numbers. It is also known that asphalts which are classified by these physical tests as being similar can vary considerably in their chemical composition. These variations in physical or chemical properties can be expected to influence the effectiveness of the asphalt as soil stabilizer.

The usual classification of asphalt cutbacks into rapid, medium, or slow curing is made according to the volatility of the solvent used in cutback preparation. The ability of these different solvents to dissolve asphalt constituents varies widely. In addition, some of these solvents tend to peptize micelles of asphaltenes in asphalt; others, flocculate them. The asphalt films obtained by evaporation of the volatile solvent from such solutions or suspensions in different fluids would, for example, be expected to behave differently on contact with liquid water or water vapor. These different cutbacks might not only waterproof the soil to differing degrees, but might also show differences in ease of distribution in wet soils.

Another factor which was kept constant throughout previous work, yet can be considered as important in stabilization of soil with asphalt cutbacks, is the ratio of asphalt to solvent in the cutback. More viscous (that is, higher asphalt content) asphalt cutbacks would mix differently with soil than the lower viscosity cutbacks. The asphalt films deposited on soil particles would vary in thickness and, therefore, in ability to waterproof the soil.

The purpose of the work described in this section was to investigate the effects of the above mentioned factors on stabilization of soil with asphalt in cutback form.

To summarize briefly, the following were investigated:

- a. Stabilization effect of different penetration asphalts derived from the same crude source.
- b. Effect of asphalts of similar penetration values, but obtained from different crude sources.
- c. Effect of varying ratio of asphalt to solvent in cutback.
- d. Effect of various solvents as asphalt cutback components.

Materials

Soil. Only one soil, namely, Massachusetts clayey silt (M-21), stored in a moist condition (moisture content = 9.5 - 10.5 percent) was used throughout these investigations.

Asphalts. Asphalts listed below were used for asphalt cutback preparation:

<u>Asphalt</u>	<u>Manufacturer</u>	<u>Crude Oil Source</u>
(1) 100/120 penetration	Esso Standard Oil Co., Everett, Mass.	Venezuela (Biechaquero Field)
(2) 85/100 penetration	Esso Standard Oil Co., Everett, Mass.	Venezuela (Biechaquero Field)
(3) 60/70 penetration	Esso Standard Oil Co., Everett, Mass.	Venezuela (Biechaquero Field)
(4) 50/60 penetration	Esso Standard Oil Co., Everett, Mass.	Venezuela (Biechaquero Field)
(5) 85/100 penetration	Esso Standard Oil Co., Baltimore, Md.	Venezuela (Lagunillas Field)
(6) 85/100 penetration	American Bituminous and Asphalt Co.	Venezuela (Boscom Field)
(7) 85/100 penetration	Lion Oil Co.	Arkansas (Smackover Field)

The first four products represent asphalts of varying viscosity, but of common

crude-origin; the last three, supplied by The Asphalt Institute, represent asphalts of equal viscosity, but differing crude-source.

Solvents. Five different solvents were used for asphalt cutback preparation. Their properties are tabulated below in order of decreasing volatility (that is, boiling point).

Solvent	Boiling Point (deg C)	Specific Gravity	Viscosity cp. (20 C)
Carbon Disulfide (CS ₂)	46.3	1.26	0.38
n-Hexane (C ₆ H ₁₄)	68.7	0.66	0.33
Carbon Tetrachloride (CCl ₄)	76.8	1.59	0.98
Gasoline	B. P. R. 38-204	0.715	0.6
Kerosene	B. P. R. 150-400	0.83	1.3

These solvents represent a broad spread in volatility, and also in asphalt-solubilizing ability. In general, the more polar solvents are the more potent asphalt solvents and asphaltene-dispersants; the order of increasing solvency of the above compounds is believed to be:



Testing Procedures

Preparation of Asphalt Cutbacks. Asphalt cutbacks were prepared by mixing predetermined amounts of asphalt and solvent and shaking these components until the asphalt appeared to be completely dissolved or dispersed. In the cases where gasoline was used as a solvent, the proportions of solvent to gasoline was done on a weight basis. The weight ratios of asphalt to gasoline used were as follows: 3:1, 2:1, 1:1, and 0.5:1. On the other hand, when other solvents were used, a volumetric ratio of asphalt to solvent was used which yielded the same volume-concentration of the solvent as 2:1 by-weight asphalt-gasoline cutback.

Preparation, Curing, and Testing of Stabilized Soil Samples. Mixing of the ingredients was carried out in a Brabender Plastograph in two stages. First, naturally wet soil was mixed for approximately three minutes with the additional water required to bring the water level up to optimum value for compaction. Then, the asphalt cutback was added and mixed with wet soil until the mixture visually appeared to be completely homogeneous. Approximately four minutes of mixing were required to obtain this condition.

Compaction of the mixture into the Harvard Miniature compaction apparatus mold was done by using double-end static compaction. Efforts were made to compact all the samples to the same density. This was difficult to achieve with mixtures where (1) the solvent in the cutback was less volatile than water (that is, Kerosene) or (2) when the amount of solvent in the cutback was considerably greater than in the "standard" asphalt-gasoline cutback (2:1 by weight). Attempts to compact the mixtures at these conditions usually resulted in great losses of fluid asphalt from the sample even when low compaction pressures were applied. In the second case (high gasoline content) this was remedied by aerating the mixture prior to compaction, and thereby evaporating the excess solvent. This procedure could not be applied when a low-volatility solvent was present, since the water would evaporate faster than the solvent. Therefore, mixtures containing kerosene were compacted to the highest possible density which did not cause significant exudation of asphalt cutback from the sample. For these reasons, samples containing kerosene are lower in density than all other samples.

All samples thus compacted were tested for unconfined compressive strength after (1) curing for 24 hours in 100 percent relative humidity, and (2) after curing for 24 hours in 100 percent relative humidity and 24 hours total immersion in water. In the case where the effects of different solvents were investigated, additional samples were made and tested for strength after four days cure at room conditions (75 F, approximately 30 percent R. H.) and subsequent 24 hours immersion in water. It was believed that under such curing conditions the effects of different solvents in the cutback would be more pronounced.

In all instances, the volatiles contents of the samples after molding, curing, and immersion in water were determined.

Results and Discussion of the Results

Effect of Different Asphalts on Stabilization of Massachusetts Clayey Silt. In order to determine the effectiveness of different asphalts on stabilization of soil, and also to study the influence of these different asphalts when they are used in conjunction with phosphorus pentoxide, two different groups of asphalts were investigated. First, the asphalts obtained from the same crude oil source but varying in hardness (penetration number) and second, the asphalts possessing the same hardness but derived from different crude oils. It was assumed that all these asphalts were manufactured using the same or similar processes, namely, steam and/or vacuum distillation. This spectrum of asphalts it is believed, provides a reasonable basis for generalizing upon the efficacy of commonly encountered straight-run asphalts as soil stabilizers.

Table 11 and Figure 6 show the effects of different penetration grade asphalts (derived from the same crude) on stabilization of Massachusetts clayey silt, with and without phosphorus pentoxide. These results show that, for given curing conditions, asphalts of different hardness, in the absence of phosphorus pentoxide, do not vary considerably in their ability to stabilize soil, although there are indications of an increase in immersed strength with increasing hardness (decreasing penetration number). Since less viscous asphalts could be expected to be distributed more easily and uniformly through soil, but at the same time, to be more rapidly displaced from soil-particle surfaces by water, the trend toward greater strength loss on immersion with the less viscous asphalts might be anticipated.

Table 11 and Figure 6 also indicate that the effects of phosphorus pentoxide are very appreciably influenced by the hardness of the asphalt. The compressive strength of samples containing phosphorous pentoxide increases with increasing hardness of the asphalt. The strengths obtained with the hardest asphalt are about 50-70 percent higher than the strengths obtained with the softest asphalt. The explanation for these effects can be based again on the differences in distribution characteristics of these different asphalts.

The more viscous asphalts do not mix as readily with fine-grained soils, with the result that a smaller fraction of the soil surface is in contact with asphalt; as a consequence, more extensive cementation of particles by phosphoric acid can take place. Provided that the asphalt is well-enough distributed to block uptake of water by the majority of the soil mass, the increased cementation will lead to increased strength on immersion.

Table 12 and Figure 7 show the stabilizing effects of the same penetration grade asphalts obtained from different crudes in the absence and presence of phosphorus pentoxide. Assuming that identical penetration numbers indicate asphalts of similar physical characteristics, it can be said that variations in chemical composition are, on the whole, responsible for the different waterproofing abilities of these asphalts.

There is, however, no apparent correlation between the as-cured and immersed strengths of soil stabilized with these different asphalts.

Incorporation of P_2O_5 with gasoline cutbacks of these four asphalts results in a marked, and roughly equivalent, improvement in physical properties of the stabilized soil.

In this case, also, asphalts which, in the absence of phosphorus pentoxide, are (as indicated by higher immersed strength of the samples) better waterproofers, in presence of phosphorus pentoxide tend to produce samples of better immersed strength. In one case (Venezuelan asphalt from Boscom Field in conjunction with phosphorus pentoxide) the sample strengths after immersion were higher than the as-cured strength. The higher strengths of immersed samples stabilized with this asphalt alone suggest that this asphalt possesses better waterproofing qualities than the other three asphalts.

These observations, in general, indicate that beneficial effects of additives such as phosphorus pentoxide are enhanced when they are used with asphalts of superior waterproofing ability, although differences between asphalts become less significant under these conditions.

concentrated cutbacks. As noted earlier, this can be attributed to poorer distribution of the more viscous cutbacks, with consequent less interference by the asphalt of interparticle cementation by phosphoric acid. Again, however, P_2O_5 significantly reduces water absorption on immersion, which suggests that this compound enhances the waterproofing action of the asphalt.

Effect of Different Cutback Solvents on Stabilization of Massachusetts Clayey Silt. The effects on soil stabilization of five different cutback solvents when used with the same asphalt are shown in Tables 14 and 15, and Figures 9 and 10. The results presented in Table 14 and Figure 9 were obtained under "normal" curing conditions; 24 hour cure at 100 percent relative humidity, and 24 hour cure and subsequent 24 hour immersion in water. At no time during these tests were the samples allowed to dry. On the other hand, the results presented in Table 15 and Figure 10 were obtained on the samples which were tested for compressive strength after four days air drying and subsequent one day immersion in water. The results shown in these tables and figures are presented in the order of decreasing volatility of the solvents. The salient features of this study can be summarized as follows:

1. The 24-hour humid-cure strength of samples stabilized with the cutbacks alone decreases as the volatility of the cutback solvent decreases; carbon disulfide is an exception, being more volatile than hexane, but yielding a weaker sample. Variations in compacted density of the treated soil parallel strength variations (that is, the strongest sample is the densest).

2. After 24-hour humid cure and 24-hour immersion, the strength of the samples fall in the same order as the humid cure strengths. Water absorption on immersion,

TABLE 14

EFFECT OF DIFFERENT SOLVENTS IN ASPHALT CUTBACK ON STABILIZATION OF MASSACHUSETTS CLAYEY SILT

Asphalt - 50/60 Penetration Grade Venezuelan Crude; Asphalt Concentration = 5% on Dry Soil

Asphalt Cutback Composition = 1.43:1 Asphalt to Solvent (by volume)

Solvent	No Additive			24 Hrs. Cure			3% P_2O_5 (on Dry Soil)			24 Hrs. Cure		
	24 Hrs. Cure (100% RH)			24 Hrs. Immersion			24 Hrs. Cure (100% RH)			24 Hrs. Immersion		
	Vol- atiles Content %	Dry Density pcf	Com- pressive Strength psi	Vol- atiles Content %	Dry Density pcf	Com- pressive Strength psi	Vol- atiles Content %	Dry Density pcf	Com- pressive Strength psi	Vol- atiles Content %	Dry Density pcf	Com- pressive Strength psi
Carbon												
Disulfide	11.3	121.1	39 \pm 1	12.7	121.9	17 \pm 1	10.1	123.9	190 \pm 2	11.2	123.8	194 \pm 2
n-Hexane	11.1	112.8	46 \pm 3	12.6	123.7	21 \pm 1	10.1	123.3	250 \pm 12	10.6	1242	233 \pm 21
Carbon												
Tetrachloride	12.6	119.9	34 \pm 1	14.5	119.7	11 \pm 1	11.9	120.5	147 \pm 9	12.5	121.3	159 \pm 7
Gasoline	11.4	120.6	28 \pm 1	13.3	119.9	11 \pm 1	10.5	120.3	201	11.3	121.3	177 \pm 6
Kerosene	13.2	114.0	28 \pm 2	15.4	115.0	6 \pm 2	11.6	117.4	76	13.0	117.0	76

All numbers in the Table are averages of two samples.

TABLE 15

EFFECT OF DIFFERENT SOLVENTS IN ASPHALT CUTBACK ON STABILIZATION OF MASSACHUSETTS CLAYEY SILT

Asphalt - 50/60 Penetration Grade Venezuelan Crude; Asphalt Concentration = 5% on Dry Soil

Asphalt Cutback Composition = 1.43:1 Asphalt to Solvent (by volume)

Curing Conditions: 4 Days Cure in Air Followed by 1 Day Immersion in Water

Solvent	No Additive					3% P_2O_5 (on Dry Soil)				
	Dry Density After Molding pcf	Volatiles Content After Molding %	Volatiles Content After Curing %	Volatiles Content After Immersion %	Compressive Strength psi	Dry Density After Molding pcf	Volatiles Content After Molding %	Volatiles Content After Curing %	Volatiles Content After Immersion %	Compressive Strength psi
Carbon										
Disulfide	124.6	11.3	1.7	9.1	91 \pm 3	123.6	11.5	4.3	5.3	505 \pm 15
n-Hexane	122.2	11.9	1.4	6.8	109 \pm 0	122.7	11.4	3.6	4.7	522 \pm 22
Carbon										
Tetrachloride	120.9	12.5	1.6	6.3	135 \pm 7	121.5	13.0	3.8	4.9	356 \pm 4
Gasoline	123.3	11.3	1.6	6.2	172 \pm 5	121.4	11.7	4.0	5.2	412 \pm 37
Kerosene	118.3	13.3	3.1	7.1	71 \pm 12	116.9	13.0	5.7	6.9	293

All numbers in the Table are averages of two samples.

4. In the presence of P_2O_5 (3 percent on soil), as-cured and immersed strengths (irrespective of cure conditions) of samples containing non-dispersing asphalt solvents (hexane, gasoline, kerosene) decrease with decreasing solvent volatility. Samples containing dispersing solvents (carbon disulfide and carbon tetrachloride) are weaker than corresponding non-dispersing solvent systems, yet show a similar decrease in strength with decreasing volatility. With non-dispersing solvents, water-absorption on immersion decreases somewhat with decreasing solvent-volatility.

The trends described above can be, to a degree, explained in terms of uniformity of asphalt-distribution of the soil, as have other results of this investigation. Considering solvents of similar chemical composition but differing volatility, the less volatile solvent will permit more uniform asphalt distribution, since the solvent will remain in the asphalt (and maintain high fluidity) longer. Considering solvents of roughly equal volatility but varying "solvency power" with asphalt, the more active solvent will facilitate better asphalt distribution by (a) producing a more fluid solution than a poor solvent at equivalent concentration, and (b) maintaining greater fluidity for a longer period during solvent evaporation. Thus, those solvents which contribute to more uniform asphalt distribution will contribute to reduced strength and higher water-absorption of the stabilized soil, this explanation satisfactorily accounts for the trends noted in items 1, 2, and 4.

The behavior of stabilized soil after dry-curing and subsequent immersion (observation 3) merits special consideration, however. With drying, shrinkage forces are developed which tend to further consolidate the soil mass. If the cutback solvent is very volatile, then the viscosity of the asphalt will increase to a high value early in the drying process, and the consolidation of the soil by water-loss will be impeded by the presence of the solid asphalt. On the other hand, if the cutback solvent is of low volatility, the asphalt will remain fluid during the larger part of the drying period, and thus not interfere with shrinkage during water evaporation. Consequently, soil stabilized with less volatile cutbacks should develop higher strength and density on drying than those stabilized with more volatile cutbacks. The fact that the kerosene-cutback system is weaker than the gasoline-cutback system is presumably due to the presence of significant residual cutback solvent in the former. In the presence of P_2O_5 , on the other hand, uniformity of asphalt distribution is the primary factor determining the degree of phosphate-cementation, so that poorer strengths are obtained with the less volatile (or more potent) solvents.

Conclusions

The following general conclusions regarding cutback stabilization of a clayey silt such as M-21 are considered justifiable, as a consequence of this study:

a. In the range of asphalt penetration numbers between 50 and 120, the compressive strength and water resistance of soil stabilized with a 2:1 asphalt-gasoline cutback and cured under humid conditions increases with increasing asphalt hardness.

b. Under conditions specified in (a), soil stabilized with cutback of high asphalt: gasoline ratio exhibits higher strength and water resistance than that stabilized with cutback or low asphalt: gasoline ratio.

c. Under conditions specified in (a), treatment of soil with asphalts of equal hardness, but differing crude-sources (cutback solvent and proportion fixed) reveals slight differences in stabilization effectiveness. These differences are, on the whole, smaller than those produced by variations in asphalt hardness, and cutback solvent type and concentration.

d. Under conditions specified in (a), cutbacks prepared with solvents of high volatility are more effective stabilizers than those prepared with low volatility solvents, provided these solvents show comparable solubilizing action on asphalt. Good asphalt solvents (that is, CS_2 , CCl_4) give poorer stabilization than poor solvents (that is, aliphatic hydrocarbons) of comparable volatility.

e. Under conditions where water can evaporate from a cutback-treated soil during cure, more volatile cutback solvents give poorer stabilization than less volatile ones.

Very low volatility solvents (such as kerosene), however, which remain behind after cure, result in inferior stabilization.

f. Addition of phosphorus pentoxide (3 percent on soil) with cutback results in an enormous (5-15 fold) increase in strength and water-resistance, irrespective of cutback composition. In general, cutbacks which, by themselves, show superior stabilizing ability are most responsive to P_2O_5 treatment.

g. The stabilizing effectiveness of an asphalt cutback appears to depend primarily on its ability to be distributed through the soil; this characteristic is determined by the initial cutback viscosity, and the rate of increase of viscosity due to solvent evaporation. Cutbacks which distribute very uniformly in soil (that is, those of low viscosity and/or low rate of evaporation) generally yield poorer results under humid cure conditions than those which distribute less uniformly.

h. Improvements resulting from P_2O_5 incorporation appear to result to a large degree from interparticle cementation involving reaction between soil and phosphoric acid. Hence, cutbacks which distribute very uniformly in soil interfere with the cementation process, and soils so treated benefit less from P_2O_5 incorporation than those treated with less readily distributed cutbacks.

i. Phosphorus pentoxide also appears to improve directly the stabilizing effectiveness of asphalt, as evidenced by its ability to reduce markedly the absorption of water by cutback-treated soil on immersion.

D. OTHER REACTIVE CHEMICAL ADDITIVES AS AIDS TO ASPHALT-CUTBACK STABILIZATION

Materials and Procedure

The objective of this study was to determine the influence of a number of reactive chemicals as additives to asphalt cutback, and to compare the results with those obtained using phosphorus pentoxide in Massachusetts clayey silt (M-21).

Soil at 11 percent moisture content was blended with 5 percent asphalt as a cutback (a 2:1 asphalt-gasoline cutback, containing 40-50 penetration, straight run asphalt (Shell HOA-2635), in which the chemical was dissolved or dispersed) in a Baker-Perkins sigmamixer for about 10 minutes. Samples were compacted via one-end static compaction in a Harvard Miniature mold to a dry density of about 120 pounds per cubic foot, cured for two weeks at ambient temperature and humidity (25 C, 30-50 percent R. H.), and totally immersed in water for one week. As-cured and immersed unconfined

TABLE 16

EFFECT OF CHEMICAL ADDITIVES ON STABILIZATION OF MASSACHUSETTS CLAYEY SILT (M-21) - BATCH A

Asphalt Content - ~5% on Dry Soil
Asphalt Cutback Composition = 2:1 Asphalt to Gasoline
Water Content at Mixing = 11% on Dry Soil

Additive	% Additive on Asphalt	14 Day Cure		14 Day Cure 7 Day Immersion	
		Com- pressive Strength psi	Residual Volatiles % on Dry Solids	Rewet Com- pressive Strength psi	Volatiles Content % on Dry Solids
Benzene Phosphonic Acid	0.5	466 \pm 0	0.4	231 \pm 3	2.8
PCl_3	0.5	386 \pm 0	1.0	182 \pm 7	6.3
$POCl_3$	0.5	449	1.1	170 \pm 3	6.7
$POCl_3$	0.5	368 \pm 12	1.0	166 \pm 4	
85% H_3PO_4	0.5	374	1.2	165 \pm 0	6.6
PCl_3	0.5	421 \pm 5	1.3	161 \pm 0	6.5
P_2O_5	0.5	485	1.2	142	7.4
$SnCl_4$	0.13	413 \pm 9	1.0	124 \pm 5	6.0
Ethyl Orthosilicate	0.5	376 \pm 30	1.0	118 \pm 2	4.9
Yellow P	0.22	372 \pm 24	0.7	84 \pm 4	6.1
CONTROL	0	340	1.1	71 \pm 2	6.7
$(C_2H_5)_2PO_4$	0.5	300	0.7	67 \pm 0	6.5
V_2O_5	0.5	462 \pm 32	0.7	60 \pm 3	7.0
Cr_2O_3	0.5	389 \pm 11	0.6	53 \pm 3	7.1
MoO_3	0.5	357 \pm 7	0.6	53 \pm 0	7.7
P_2O_5 + Excess CaO	0.5	490	1.3	48 \pm 3	13.1
P_2S_5	0.6	355	0.8	25 \pm 2	10.2

compressive strengths were determined in duplicate on all formulations, as were volatiles contents at test.

Two different batches of soil were used in this investigation, which exhibited significant differences in strength. Since control-samples (asphalt-stabilized, but without chemical additive) were run on each batch, the effects of chemical treatment can be satisfactorily compared within each series.

Results

Tables 16 and 17 show the effects of the various additives upon the as cured and immersed strength, and volatiles content, of the cutback stabilized soil. The treatments are listed in order of decreasing immersed strength for each soil batch.

Discussion

The results indicate clearly that all the acidic phosphorus compounds examined are markedly beneficial to asphalt stabilization. It will be noted that the phosphorus chlorides, oxychlorides, P_2O_5 , and 85 percent phosphoric acid are roughly equivalent in their action, although the oil-soluble compounds (the chlorides and oxychlorides) and liquid H_3PO_4 are somewhat more beneficial than P_2O_5 . Inasmuch as all these compounds hydrolyze rapidly to phosphoric acid on contact with water, it is believed that phosphoric acid is the ultimate stabilizing aid in all cases; such differences that do exist are probably attributable to differences in uniformity of distribution of the phosphoric acid through the soil. It is also of interest that the method of incorporation of 85 percent phosphoric acid in the soil (either dispersed in the asphalt, or used to pretreat the wet soil) has no significant effect on the ultimate strength of the product. This may be construed to indicate that the primary reaction of the acid is with the soil rather than the asphalt, and hence that particle-cementation is the more important part of its stabilizing action. It will also be noted that non-acidic, relatively stable phosphorus compounds (that is, triethyl phosphate, or P_2S_5) are virtually ineffective as stabilizing aids. While it was expected that yellow phosphorus would have been as effective as phosphoric acid as a stabilizing aid, the results indicate to the contrary; the reason for this is obscure.

Of particular importance is the outstanding beneficial action of benzene phosphonic acid (manufactured by Victor Chemical Works), which is the most effective of all additives studied.

TABLE 17

EFFECT OF CHEMICAL ADDITIVES ON STABILIZATION OF MASSACHUSETTS CLAYEY SILT
(M-21) - BATCH B

Asphalt Content ~ 5% on Dry Soil
Asphalt Cutback Composition = 2:1 Asphalt to Gasoline
Water Content at Mixing = 11% on Dry Soil

Additive	% Additive on Soil	14 Day Cure		14 Day Cure 7 Day Immersion	
		Com- pressive Strength psi	Residual Volatiles % on Dry Solids	Rewet Com- pressive Strength psi	Volatiles Content % on Dry Solids
Benzene Phosphonic Acid	0.4	379 + 7	0.6	206 +10	4.4
Benzene Phosphonic Acid	0.25	392 + 1	1.1	150 + 1	4.8
CrO ₃	0.5	477 +20	0.9	132 + 0	4.8
85% H ₃ PO ₄	0.5	481 +10	1.0	118 + 6	6.7
85% H ₃ PO ₄ *	0.5	447 +16	1.0	118 + 0	5.5
Meta-Nitrobenzoic Acid	0.5	338 + 0	0.7	110 + 0	5.7
Hydrochloric Acid	0.5	404 + 0	1.1	99 + 3	5.8
Fumaric Acid	0.5	410 + 4	0.9	95 +15	4.9
SbCl ₅	0.5	398 +27	1.2	78 + 5	7.2
Phthalic Anhydrite	0.5	422 + 0	0.8	63 + 9	8.0
CONTROL	0	482 +14	1.0	55 + 3	6.7
Benzoic Acid	0.5	388 +12	0.9	54 + 1	5.5
KMnO ₄	0.5	434 +20	1.2	50 + 2	10.5
KH ₂ PO ₄	0.5	437 +20	0.8	50 + 2	9.0
CrPO ₄	0.5	437 +14	0.9	49 + 0	7.0
Adipic Acid	0.5	322 +18	0.8	38 + 4	9.8

*Additive mixed with soil prior to addition of cutback.

A clue to the unusual activity of this compound may lie in the very low water-absorption on immersion of soils stabilized containing it; it is believed that this compound not only causes interparticle cementation characteristic of acidic phosphorus compounds generally, but also forms a hydrophobic monolayer on the soil which both improves asphalt-adhesion and reduces water-imbibition. Unfortunately, the current high cost of this compound would appear to make it economically unattractive for soil stabilization.

Of acidic compounds of elements related to phosphorus in the atomic table (chromium, molybdenum, antimony, vanadium, silicon) only chromium trioxide, and to a lesser extent, ethyl orthosilicate, are active. The former compound is second only to benzene phosphonic acid, while the latter is less active than phosphoric acid. Once again, however, economics strongly favors phosphoric acid over these compounds.

An important observation to be made from Table 17 relates to the effect of various organic and inorganic acids on asphalt-stabilized soil. Relatively strong acids (that is, those with ionization constants greater than 10^{-3}) exert a stabilizing effect, while weak organic acids do not. While phosphoric acid occupies a unique position in the list of acids, the fact remains that m-nitrobenzoic and hydrochloric acids also exert a marked beneficial action on asphalt-stabilized soil. Inasmuch as earlier work (2) has shown that hydrochloric acid is far inferior to phosphoric as a primary soil-stabilizer, it would appear that the primary function of strong acids on asphalt-stabilized soil is to improve the stabilizing (that is, waterproofing) ability of asphalt. This belief is supported by the reduction in water-absorption on immersion which results from incorporation of these compounds. It seems reasonable to postulate, therefore, that reaction of strong acids with nitrogen bases present in asphalt results in the formation of salts which function as antistripping additives. This would account for the general observation that the presence of phosphoric acid (and other strong acids) in asphalt-treated soil inevitably results in visually better coverage of the soil by the asphalt. The additional ability of phosphoric acid to function as an interparticle cementing agent can thus account for its unusual action in soil-asphalt-systems.

Conclusions

- a. Many acidic phosphorus compounds, yielding ultimately phosphoric acid on hydrolysis, are comparable or superior to P_2O_5 as aids to asphalt-stabilization. Phosphoric acid itself (85 percent) is the most economically attractive compound for this purpose.
- b. Benzene phosphonic acid is the most effective stabilization aid so far found.
- c. Chromium trioxide and ethyl orthosilicate aid asphalt stabilization significantly, but do not appear economically competitive with phosphoric acid.
- d. Strong organic and inorganic acids (in particular, hydrochloric acid) are effective stabilization aids, although inferior to phosphoric acid. Their action appears to result from reaction with asphalt components to form antistripping additives in situ. The low cost of hydrochloric acid makes this compound an interesting prospect for further study.

GENERAL OBSERVATIONS AND CONCLUSIONS

If the results reported in Section 3 are carefully examined with an eye to elucidate the mechanisms of asphalt-and-additive stabilization of soils, the following general trends will be found:

1. Incorporation of low concentrations (5 percent by weight) asphalt cutback into relatively coarse soils increases greatly the unconfined compressive strength, while incorporation into relatively fine soils reduces dry strength. Increasing asphalt concentration from 5 percent to 10 percent on the soil reduces dry strength in all cases.
2. Incorporation of asphalt cutback in soils causes improvements in wet-strength which (a) vary directly with the asphalt concentration, and (b) vary directly with the mean particle size of the soil. The wet-strength of asphalt cutback stabilized soil correlates very well with water-absorption on immersion.
3. Incorporation of fatty amines with cutback-stabilized, relatively coarse grained

soils reduces dry strength relative to treatment with unmodified cutback; with fine-grained soils, the reverse occurs.

4. Incorporation of fatty amines with cutback stabilized soils results in a significant improvement in wet-strength. The improvements are in all cases paralleled by a corresponding reduction in water-absorption on immersion, and are apparent immediately upon compaction; that is, no "curing period" is required to develop the strength-improvements.

5. Incorporation of phosphorus pentoxide (or related compounds) with cutback stabilized soils causes dry-strength increases with relatively coarse soils, but has little consistent effect upon dry strength of fine-grained soils.

6. Incorporation of phosphorus pentoxide with cutback stabilized soils causes very large improvements in wet-strength, and corresponding large reductions in water absorption on immersion. Such soils also undergo increases in strength on aging in air, and in many cases, under water. Soils treated with phosphorus pentoxide alone, when allowed to cure sufficiently, develop appreciable wet-strength, but, in contrast, absorb large amounts of water on immersion.

7. Incorporation of phosphorus pentoxide and amine with asphalt cutback causes substantial improvements in wet-strength (over that produced by either additive alone) of relatively fine-grained soils, but not of coarse-grained soils. Soils which benefit from the dual-treatment also show a further reduction in water-absorption on immersion.

8. Conditions which favor very uniform distribution of asphalt through a fine-grained soil (that is, dilute cutbacks, low viscosity asphalts, low-volatility or high dispersing cutback solvents) appear to reduce the wet-strength, and increase water-absorption by the treated soil.

In an effort to explain these observations, the following hypothesis of interaction of asphalt, additives, and soils is proposed.

When a wet, cohesive soil is blended with a representative concentration of asphalt cutback, the total quantity of fluid present initially is usually greater than that necessary to fill completely the soil voids on compaction. During mixing, the non-wetting cutback phase is dispersed as globular or filamentitious masses between the soil particles or particle-aggregates; the degree of subdivision of the cutback (as measured by the mean globule-size and uniformity of cutback distribution between soil particles) and of breakdown of soil-aggregates, is evidently dependent on the duration and intensity of the mixing process. Upon molding and compaction of the mixture, the free void space is reduced, part of the volatile fluids (water and cutback solvent) are lost by evaporation, and the dispersed cutback particles are squeezed out into filaments and laminae which occupy a rather large fraction of the void space. Because of capillary forces, the asphalt phase will be confined to the larger pores and/or channels, while water will occupy the fine-texture porosity of the mass. The resulting mixture may, therefore, be considered as a close-packed mass of water-wet particles and aggregates surrounded by a partially continuous network of asphalt, as shown in Figure 11. When the mass is dried, shrinkage causes some additional distribution of the asphalt, but this is opposed by reduction in asphalt-volume and increase in viscosity due to cutback solvent evaporation. If the soil is itself of low cohesiveness, the adhesion of the asphalt to the soil on evaporation of water will result in the development of cohesion of the mass, and the magnitude of the strength developed would be expected to be roughly proportional to the fraction of the void space filled with asphalt. If, on the other hand, the soil is a highly cohesive one, then the presence of asphalt in the voids will interfere with the formation on drying of soil-soil bonds which are far higher in strength than soil-asphalt bonds; hence the presence of asphalt will reduce the dry strength.

When a cutback-treated soil is immersed in water, capillary forces tend to draw water into the mass via those pores and channels which are open and exposed to the liquid. Since the larger pores are filled with asphalt, and since many elements of the soil mass are probably surrounded or encapsulated by asphalt, both the rate of water-imbibition, and the ultimate water-saturation are significantly less than that of untreated soil. The probability that a pore will be plugged by asphalt, or that a soil-

element will be encapsulated, will increase as a number of pores per unit volume, or particle surface area per unit mass, decreases; hence, it would be expected that coarser soils would undergo less strength-loss on rewetting than finer soils. Similarly, loss in strength on immersion would be expected to decrease with increasing asphalt concentration.

After cutback-solvent evaporation has occurred in a fine-grained soil, the asphalt itself occupies a relatively small fraction (typically, about a third) of the void space. In order to develop significant water-resistance, the asphalt must be distributed in a fashion that will block, to the greatest possible degree, water-uptake by the soil. This can be most satisfactorily accomplished if the asphalt is consumed in surrounding, as protective sheaths, relatively large agglomerates of (essentially asphalt-free) soil particles. This condition is certainly far better than that which would obtain if the asphalt were "perfectly" distributed, wherein one of every three pore-spaces in the soil would be filled with asphalt. One is, therefore, led to the conclusion that there may be an optimum level of distribution if asphalt in a cohesive soil, both below and above which water-uptake by the soil is increased. Attainment of this "optimum" level of distribution can evidently be facilitated by (a) using an asphalt-cutback solvent combination sufficiently viscous to prevent excessive subdivision during mixing, or (b) stabilizing soil-aggregates to that they remain intact during mixing.

Another factor of obvious importance in asphalt stabilization is the mobility of the asphalt within the soil. If, after curing or drying, the asphalt remains quite fluid, then capillary movement of water into the soil will tend to displace the asphalt and facilitate water-entry. This, therefore, constitutes another reason why high-viscosity asphalts appear to be better stabilizers for fine-grained soils that more fluid ones.

When a fine-grained soil is treated with asphalt cutback and an antistripping additive such as a primary amine, two important changes occur in the system: (1) the soil surfaces are rendered asphalt-wettable, and (2) the fine soil particles are caused to agglomerate. The first phenomenon leads to true "water-proofing" of soil particles, and to the distribution of cutback in predominantly laminar (rather than globular) form, with the result that complete encapsulation of particles and aggregates by asphalt is much more likely to occur than with asphalt alone. The second phenomenon tends to retard aggregate-breakdown on mixing, and thus to confine the asphalt to the aggregate surfaces. The resulting structure can be envisioned as a virtually continuous laminar network of asphalt surrounding nearly asphalt-free soil aggregates (Figure 11). Such a system would be expected to exhibit much higher resistance to water-attack than that obtained with unmodified cutback.

The wet compressive strength of asphalt-stabilized soils is evidently determined primarily by the compressive strength of the encapsulated aggregates within the mass. The strongest evidence supporting this belief is the previously determined observation (1) that the rewet compressive strength of asphalt stabilized soils is dependent almost entirely on the water absorption by the soil, and virtually independent of such factors as asphalt type and concentration, presence of waterproofing additives, curing conditions, and the like.

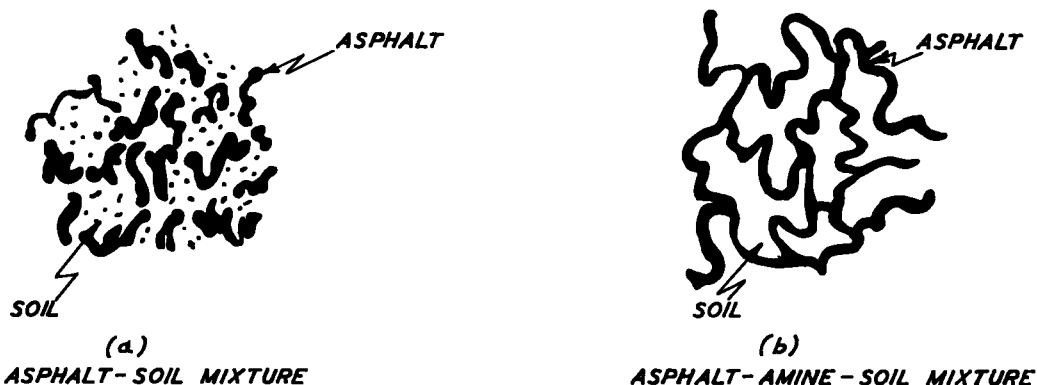


Figure 11.

If this is the case, then any reaction or process occurring within the soil which tends to increase the wet compressive strength of the aggregates should also increase the gross strength of the stabilized soil. Furthermore, enhancement of aggregate-strength, by preventing displacement of particles with the aggregates, will also tend to reduce swelling of the soil on water imbibition, and hence, water-absorption. The role of acidic phosphorus compounds in enhancing wet strength of asphalt-stabilized soils appears primarily (but not solely) to be one of aggregate-solidification. Inasmuch as the cementing action of these additives involves reaction with "clean" (that is, uncoated) soil particles, the dry strength of soils so treated will depend on the degree of interference to bonding caused by the asphalt. Since fine-grained soil stabilized with phosphoric acid alone is much stronger when dry than untreated soil, whereas asphalt-treated soil is much weaker, the net change in dry strength brought about when both substances are present cannot be predicted with certainty. With coarse-grained soils, however, both substances above have been shown to enhance dry strength, hence the combination would be expected to do so also.

It has been noted that soils treated with phosphoric acid or related compounds are rendered more fluid for a given water-content than untreated soils, which indicated that these additives exert a dispersing or dis-aggregating effect on the soils. Such a dispersing action, by itself, would be expected to be detrimental to asphalt stabilization for reasons mentioned above. This effect would, therefore, tend to reduce the wet-strength of phosphoric-asphalt treated soils to a value lower than that possible when well-aggregated soil. With coarse-grained soils, this reduction would probably not be of much consequence, but with very fine-grained soils the loss in strength due to dispersion may be very great indeed. When, however, a fatty amine is added to such a system, the dispersive action of the phosphoric acid is to a large extent eliminated, and new aggregates are formed (2). The consequence of this would be improved utilization of the asphalt in aggregate-encapsulation, reduced water-absorption in immersion, and improved wet strength. The response of fine-grained asphalt-stabilized soils to dual treatment with acidic phosphorus compounds and amines can thus be reconciled.

One of the most convincing demonstrations of the importance of aggregate-formation and solidification in asphalt stabilization of fine-grained soils is offered by the following series of tests:

Vicksburg buckshot clay, at its optimum water content for compaction, was pretreated with trace-quantities of two compounds known to flocculate clays and stabilize clay aggregates. These compounds were (a) ferric chloride, and (b) a cationic polyelectrolyte (a quaternized aminoethyl acrylate provided by the duPont Company). After treatment, the soil was either (1) blended with asphalt cutback, or (2) air-dried to low moisture content, then rewet and blended with cutback. Comparative strength and water-absorption data of samples prepared in this fashion are shown in Table 18.

It will be noted that ferric chloride treatment, while ineffective in aiding development in wet-strength when asphalt incorporation is performed with the wet soil, causes significant strength-retention on immersion when the soil is subjected to an intermediate

TABLE 18

EFFECT OF AGGREGANT-TREATMENT ON ASPHALT CUTBACK STABILIZED VICKSBURG BUCKSHOT CLAY

Asphalt Concentration = 10% on Dry Soil
Cutback Composition = 2:1 Asphalt to Gasoline

Additive and Concen- tration % on Soil	At Molding		14 Days Cure			7 Days Water Immersion		
	Vol- atiles Content %	Density lb/ft ³	Vol- atiles Content %	Density lb/ft ³	Com- pressive Strength psi	Vol- atiles Content %	Water Absorp- tion %	Com- pressive Strength psi
None	20.8	94.0	3.0	107.0	502 ⁺⁶⁴	Samples Disintegrated		
FeCl ₃ (0.2)	20.3	94.1	3.3	106.0	537 ⁺²⁰			
FeCl ₃ (0.2) ¹	19.3	97.3	2.9	107.4	447 ⁺³⁵	20.3	16.6 ^{+0.1}	97.3
Polymer (0.2)	21.1	93.4	2.8	105.0	449 ⁺³⁰	24.7	21.0 ^{+0.1}	21 ^{+ 2}
Polymer (0.2) ¹	19.6	98.0	3.0	108.8	458 ⁺³⁷	13.7	11.0 ^{+0.1}	13 ^{+ 0}
							99.4	79 - 9

¹Dried

drying process prior to asphalt-incorporation. Although ferric salts tend to cause aggragation of wet clays, the strength and water-resistance of the aggregates produced is greatly increased on drying, evidently due to particle cementation via hydrous iron oxides. With the polymeric flocculant, however, the stability of the aggregates produced initially is reasonably high, and further stability developed on drying is marked; hence, the wet-strength of the asphalt stabilized soil is measurable without intermediate drying, and substantial with it. The low water-absorption of the polymer-treated, asphalt stabilized soil (with intermediate drying) is an excellent indication of the water-resistance of the aggregates, and their effective encapsulation.

The most important deduction to be made from this analysis is that most satisfactory asphalt stabilization of fine-grained soils is achieved when the "effective" particle size of the soil is increased (by flocculation or cementation) to a level approaching that of a coarse-grained soil. This implies that successful asphalt-stabilization of heavy soils will greatly benefit by the use of secondary flocculating or cementing additives, except in those circumstances where highly agglomerated clayey soils are encountered.

A few comments relative to the economics of cutback-stabilization of fine-grained soils would seem appropriate at this point. A representative formulation which would be expected to stabilize adequately a moderately fine-grained soil is as follows:

Material	Concentration, lb/100 lb soil	Approx. Cost/lb \$	Cost/100 lb soil \$
Asphalt	5.0	0.01	0.05
Cutback Solvent	2.5	0.02	0.05
Amine	0.2	0.25	0.05
Phosphoric Acid	1.0	0.06	0.06
		Total	0.21

Total materials cost, therefore, comes to 21 cents per 100 lb of soil, or roughly \$5.70 per cubic yard. At this figure, asphalt-stabilized soil cannot compete with coarse aggregate in, for example, highway subgrade applications, at least on a yard-for-yard basis, but does compare favorably with that of the same soil stabilized with 10 percent portland cement. Comparison on a yard-for-yard basis is, at best, misleading, since it fails to consider differences in structural properties of the products. Asphalt-and-cement-stabilized soils both differ from coarse aggregate in being cohesive materials, and hence may be required in lesser amounts to develop satisfactory load-bearing strength. Asphalt-stabilized soil differs from cement-stabilized soil in that (a) it exhibits some resiliency, and (b) it absorbs relatively small amounts of water, and has relatively low water permeability. These properties might prove advantageous in road subgrade preparation where resistance to cracking and freeze-thaw deterioration is important, and where a water-impermeable blanket below the base-course is desirable. These same properties of asphalt-stabilized soils may also render attractive their use as low-cost secondary-road surfacing materials, for earth housing, for irrigation ditch lining, and the like. In any case, the cost of chemically modified, asphalt-stabilized soils lies in a range of practical interest in heavy construction applications; hence, these products would appear to merit thorough field-evaluation.

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