A LABORATORY STUDY OF THE SOIL STABILIZING EFFECTIVENESS OF ARTIFICIAL RESINS WITH SPECIAL EMPHASIS ON THE ANILINE-FURFURAL RESINS

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A LABORATORY STUDY OF THE SOIL STABILIZING EFFECTIVENESS OF ARTIFICIAL RESINS WITH SPECIAL EMPHASIS ON THE ANILINE-FURFURAL RESINS

SUMMARY

This report presents the data obtained from a laboratory investigation of the soil stabilizing properties of numerous artificial resins. Because of their outstanding effectiveness, the resins formed by the reaction of aniline and furfural were given special attention.

For practically all of the exploratory work proper, the compressive strength of 2" x 2" compacted soil cylinders, after exposure to different types of laboratory weathering, were used as a criterion of the effectiveness of the various resin treatments. In the evaluation of the effectiveness of one aniline-furfural resin with ten different soils, load-plunger tests were performed on 4^{μ} x 6^{μ} cylinders in addition to the compression tests on the small specimens

Experiments in which the ratio of aniline to furfural was varied indicated that the resin formed by the reaction of 70 parts of aniline and 30 parts of furfural was the most effective stabilizer. This resin gave best results when formed in a neutral or slightly acid medium and was improved by the addition of iron or aluminum salts

Quantities of aniline-furfural resin (ratio 70 30) as small as 2 percent on the basis of the dry weight of soil treated were effective in stabilizing most of the 10 different soils tested. It was found that this material acted both as a binding and as a waterproofing agent for the compacted soils. That these properties are of significant magnitude is demonstrated by comparing data from tests on various types of stabilizers.

Urea-furfural, phenol-furfural, and phenol-formaldehyde mixtures were found ineffective as soil stabilizing agents. Urea-formaldehyde and calcium sulfamate treated specimens showed some promise but the experiments performed were not conclusive

A discussion of the history and structure of aniline-furfural resins and the results of a series of experiments concerning the catalyzation of these materials are given in the Appendixes

INTRODUCTION

The war-time investigations in soil stabilization sponsored by the Technical Development Division, Civil Aeronautics Administration, have emphasized the use of local materials available in combat areas, and the development of superactive stabilizers that would achieve with small quantities the same results as the relatively large quantities employed in the case of conventional methods. The stabilizing effectiveness of rosin and its derivatives has been studied and the results have been previously reported 1 Another group of materials that appeared to be of sufficient promise to merit investigation was that of artificial resins

lWinterkorn, Hans F and McAlpin, George W, "Soil Stabilization by the Use of Rosin," CAA Technical Development Note No 34, McAlpin, George W, Mainfort, Robert C, and Winterkorn, Hans F, "A Laboratory Study of the Soil Stabilizing Effectiveness of a Complex Salt of Abietic Acid," CAA Technical Development Note No 35

The possible usefulness of artificial resins for highway construction was realized in the early thirties and exploratory investigations were made concerning the following possible applications of such materials 2

- 1 The possible use for high-type pavements of plastics made of artificial resins and natural soil as filler.
- 2 The stabilization of soils by means of artificial resins to serve as base courses for highway and airport pavements,
- 3 The activation of conventional soil stabilizing materials, such as bitumen, by means of artificial resins, to improve the quality and economic life of stabilized base courses;
- 4 The improvement of the stripping resistance of bitumen coated mineral aggregate by means of artificial resins

Each of these studies disclosed interesting and pertinent data concerning the applicability of these materials. The last of these subjects was pushed to practical application with satisfactory results 3. Those data resulting from this previous work which deal most directly with the treatment of soils may be summarized as follows.

- 1 Of the lower priced artificial resins such as urea-formaldehyde, urea-furfural, aniline-furfural, and aniline-formaldehyde, the resin made of about 2 parts of aniline and 1 part of furfural was the most effective for soil stabilization and as a precoating for aggregate to increase its affinity for bitumen,4
- 2 About two percent of this resin on the basis of the weight of the dry soil was required for effective soil stabilization at the relatively low densities employed before the advent of even the Proctor method. The use of smaller amounts, however, considerably improved the physical properties of the soil investigated. The effectiveness of the aniline-furfural resin did not appear to be lessened in alkaline soils, which usually react badly with bitumen;
- 3 If used as an activator for bitumen in soil stabilization only about 2 percent of the material, on the basis of the weight of the bitumen were required. The latter amount usually ranges between 5 and 8 percent of the dry weight of the soil

; This formula well indicates the polar nature of this substance which makes it easily adsorbed by the soil particles, and also explains its dark red color

Winterkorn, Hans F, unpublished notes

³Winterkorn, Hans F. "Affinity of Hydrophilic Aggregate for Asphaltic Bitumen, Use of Furfural and Its Resinous Derivatives for Improving Affinity," Ind. and Eng Chem, 30, pp 1362-68, 1938 (U S Patent No. 2,314,181 Granted March 16, 1943)

⁴The probable molecular structure of this resin according to the literature and our own experiments is

With the results of these earlier studies as a background, the Civil Aeronautics Administration inaugurated an investigation of the soil stabilizing effectiveness of artificial resins. This study, the results of which are presented herein, was conducted under the direction of Dr. Hans F. Winterkorn in the Soil Mechanics Laboratory of the University of Missouri and in the Soil Science Laboratory of Princeton University, assisted by Rollie G. Fehrman, I George Morrison, and Henry Walter. The work was supervised for the Airport Development Section of the Civil Aeronautics Administration by George N. McAlpin

DESCRIPTION OF MATERIALS

Ten soils, representing textural differences from sand to silty clay, were employed for this investigation. Their physical and chemical characteristics are given in table 1. Figure 1 shows the grain-size distribution curves of the soils. Only the material passing the No. 10 sieve was used in making the test specimens.

The chemicals used were of C P quality except the aniline and furfural which were of commercial grades Distilled water was used in all laboratory experiments

PROCEDURES FOR PREPARING AND TESTING OF SPECIMENS

Two sizes of specimens were used during the investigation, viz, 2" x 2" and 4" x 6" compacted soil cylinders. Practically all of the exploratory and research work proper was done with the small cylinders. The moisture content-density relationship of the soils was determined by the standard Proctor compaction procedure (A A S H O T99-38) with the exception that the size of specimens employed was 4 inches in diameter and 6 inches high (standard specimen is 4" x 4 59"). The consequence of this modification was, of course, a lowered maximum density. The density of these specimens must therefore be kept in mind in evaluating the test data. Work with other stabilizing agents has shown that specimens compacted to the higher static-load density (2000 psi) may be as much as four times as stable as specimens of the same materials compacted to the Proctor density.

In molding the larger test specimens, the optimum moisture content of the soils, as found by the modified compaction procedure given above, was employed. Because of the low compactive effort used and the low densities obtained, difficulty was encountered in forming specimens with the desired properties. These difficulties were magnified in the case of the smaller test specimens occause of the small volume of soil employed Fortunately, these variations do not seem to affect disadvantageously the conclusions which can be drawn from the respective experiments

The design values for dry densities and moisture content of compaction as well as the average of the actual values obtained for the $4" \times 6"$ and $2" \times 2"$ specimens, are given in the following table

	Planned P	roperties	Obtained Properties						
			4"x 6" S	pecimens	2"x 2" 5p	ecimens			
Soll	Moisture %	Dry Density Lb/Cu Ft	Moisture %	Dry Density Lb/Cu Ft	Moisture	Dry Density Lb/Cu Ft			
HP BE LG WMN V	12 14 14 5 14 15 16 17 22 28	103 109 113 5 115 116 110 110 104 96 90	10 15 14 5 15 15 16 17 17 21	103 110 115 5 114 5 115 112 109 104 98 96	9 8 12 13.5 16 16 12 12 5 16 18 5 28 5	96 107 116 106 106 114 102 103 106 96			

2" by 2" Specimens

Enough air-dried soil to make twelve 2-inch specimens was weighed out into the mixing pan The soil was divided into two equal portions; one of the resin forming ingredients together with the amount of water to give one-half of the optimum moisture content was thoroughly mixed into each portion Just before the compaction the two portions were combined and thoroughly mixed

The specimens were made by means of a compaction apparatus adopted from the testing of foundry sands and first used for soil stabilization testing by the Portland Cement Association The apparatus permits uniform densification from both top and bottom, the specimen being compacted in a floating ring.

All compacted specimens were air-dried for 7 days Duplicate specimens were then subjected to each of the following variations in exposure, after which their compressive strength was determined

- No further exposure
- 2. Two-hours immersion in water
- 3. One-cycle of wetting and drying⁵
- 4. Four-cycles of wetting and drying
- 5. One-cycle of freezing and thawing6 Four-cycles of freezing and thawing

4" by 6" Specimens

The soil plus the required percentage of water to produce the desired density, together with the stabilizer to be employed, were combined and compacted The resulting wet soil cylinders were extruded from the mold, carefully weighed, air-dried for 3 days, and then dried in an oven at 70° C to constant weight. Three identical specimens were then subjected to each of the following variations of exposure

- No further exposure
- 10 days capillary absorption7
- 10 days capillary absorption and re-drying in an oven to constant weight
- 12 cycles freezing and thawing8
- 12 cycles freezing and thawing and re-drying in an oven to constant weight
- 12 cycles wetting and drying9
- 12 cycles wetting and drying and re-drying in an oven to constant weight

One wet-dry cycle consisted of 5 hours immersion in water followed by 43 hours ovendrying at 70° C For both the 1 and 4 cycle exposures, the specimens were immersed in water for 2 hours just before being tested for compressive strength

One freeze-thaw cycle consisted of 2 hours immersion in water followed by 24 hours freezing at -10° F and 24 hours thawing in a moist room For both the 1 and 4 cycle exposures, the specimens were immersed in water for 2 hours just before being tested for compressive strength

⁷Specimens were placed on a bed of moist sand

⁸Specimens were first subjected to 10 days capillary absorption. One cycle of freezing and thawing consisted of placing the specimens in a cold room (-10° F) for a period of 8 hours with subsequent thawing in a moist room (70° F - relative humidity 95-100 percent) for 16 hours. Twelve such cycles constituted a freezing and thawing test

Specimens were first subjected to 10 days capillary absorption. One cycle of wetting and drying consisted of placing the specimens for 12 hours in a water bath at room temperature, so that the water level of the bath was 1 inch below the top of the cylinder, with subsequent re-drying in an oven (70° C) for 36 hours. Twelve such cycles constituted a wetting and drying test

After each of these types of exposure, the unconfined specimens were placed upright under the head of a testing machine to which was fastened a metal plunger 2 inches long, machined so as to have a circular head with an area of 0.75 square inches. This plunger was placed concentrically on the specimen. After seating of the plunger, load was applied at the rate of 400 pounds per minute until the specimen failed or a penetration of 0.1 inch was obtained. The load and penetration values for 3 identical specimens were averaged and reported for each combination and treatment.

TEST RESULTS I -- ANILINE-FURFURAL RESINS

For the general study of the basic factors influencing the soil stabilizing properties of aniline-furfural resins the previously described compressive strength test on 2 inch by 2 inch specimens was used. One soil, Nimitz fine sand - designated as "soil H" in this report - was used for most of these tests

For the specific evaluation of the effectiveness of the 70 30 aniline-furfural resin with 10 different soils, both the compressive strength test on the small specimens and the plunger test on the 4 inch by 6 inch specimens were employed. The complete data obtained in these tests are presented in tabular form. For the purpose of simplifying this presentation, the effect of the different types of treatment upon the compressive strength of the air-dried specimens and of those that had been immersed in water for 2 hours has been shown graphically. Observations based upon the strength values of the air-dried specimens may be open to question inasmuch as the air temperature and humidity during the curing period varied considerably. They do, however, indicate general trends that are of value in analyzing the data. The results obtained from the wetting-drying and freezing-thawing tests have not been plotted since they, in general, give the same picture as the "wet" data.

The Effect of the Anıline-Furfural Ratio on the Quality of the Resinous Cement in Acid, Alkaline and Neutral Media

The strength data obtained in these tests are shown in figure 2 and in tables 2, 3, 4 and 5. It will be noted that a definite maximum of compressive strength is obtained, which, in all cases except that in which 3 cc of concentrated HCl (hydrochloric acid) were used as a catalyst, comes at a composition of about 70 parts of aniline to 30 parts of furfural In the case of the addition of 3 cc of concentrated HCl the curve shows a maximum at a composition of 1 part of aniline to 1 part of furfural The dry strength curves point to the possible existence of three resin compounds corresponding to compositions of 50 50, 70 30, and 35 65 parts of aniline and of furfural, respectively This impression, however, must be corrected on the basis of the showing in the "wet" test It will be observed that the curve of the neutral specimens shows the highest value for compressive strength and that this value comes at a ratio of 70.30 However, upon the addition of 1 5 cc HCl (0 08% by weight of the dry soil per batch - 12 specimens) the maximum is moved to a ratio of about 2 1 and the best compressive strength obtained is considerably less than that obtained in a neutral medium If more HCl is added (3 cc or 0 16%), the compressive strength further decreases, and the peak of the curve is moved to a ratio of about 1 1 It will also be noticed that though the peak of the curve is lower, the strength of the specimens is less affected by changes in the ratio of the aniline-furfural mixture than in either of the less acid mixtures The alkaline specimens turned out very badly Fowever, the best mixture was around the ratio of 70 30 parts of aniline and furfural, respectively

It is interesting to note that the tests in which specimens were soaked in water gave no indication of a strength maximum at a ratio of 35 parts of aniline to 65 parts of furfural as was found in the specimens tested dry. This would indicate that, if a resin might be formed at this ratio, it definitely does not stand weathering

The Effect of Hydrogen and Hydroxyl Ions on Three Aniline-Furfural Resins

The results of tests to determine the effect of hydrogen and hydroxyl ions on the properties of aniline-furfural resins are given in figure 3 and in tables 6, 7, and 8. The data and curves marked dry represent the specimens tested directly after curing without weathering treatment, while the data and curves marked wet are for specimens subjected to two hours' immersion in water. It should be noticed that none of the resin binders did as well in alkaline specimens as in neutral or acid specimens. The wet test curve for the 70 30 resin shows a sharp rise in strength in the most alkaline specimens indicating the possible catalytic effect of strong alkali

The 50 50 resin turned out to be very weak and unable to withstand weathering conditions

The 70 30 and 35 65 resins both showed a maximum strength slightly on the acid side with the 35.65 resin being by far the weaker of the two and the most favorably affected by the acid treatment

The Effectiveness of Low Percentages of Aniline-Furfural Resins

The results of the respective tests are given in figure 4 and in tables 9 and 10. At the specimen densities employed no appreciable weathering resistance was obtained with the 70 30 resin binder unless two percent or greater were used. Weathering resistance of specimens containing two percent of the 35 65 resin was quite low

The Effect of Various Ions on the Quality of Two Aniline-Furfural Resins

Different Anions

The respective data are given in figure 6 and in tables 11 and 12. The dotted line gives the strength after two hours' immersion - no catalyst added. Addition of H2SO4 (sulfuric acid) gave best results on the 70 30 resin binder while addition of H3PO4 (phosphoric acid) gave best results on the 35 65 resin binder. None of the admixtures resulted in great improvement, the acetic acid (CH3COOH) seemed to have even a detrimental effect on the 70 30 resin

Various Amounts of H2504

Since it appeared to be the non-volatile acids (see the paragraph above) that produced the best results in the anion tests, specimens were prepared using various amounts of H2SO4 as catalyst (tables 13 and 14). Figure 5 shows the results of these tests. It should be noticed that the curves on this figure for the wet strengths are very similar to those in figure 3 — the peak of the curves coming slightly on the acid side, then declining again with increasing acidity of the medium. This fact might indicate that the values obtained in both the H2SO4 test and the anion tests are functions of the acidity rather than of the specific character of the anion added. However, in all cases of inorganic admixtures the water affinity of the resulting reaction products must be considered.

Different Cations

The respective data are given in figure 8 and in tables 11 and 12. None of the cation treatments produced strengths nearly as good as those of the control specimens in which aniline-furfural alone was used. This result is more than likely due to the fact that the cationic compounds were added in the form of hydroxides, it has already been noted (figure 3) that none of the aniline-furfural resins developed its greatest effectiveness in alkaline mixtures.

Different Salts

In the case of the salt admixtures, it is difficult to estimate how much of the effect is due to the resulting acidity or alkalinity caused by the reaction of the salt with the system as a whole. Figure 7 shows the results of experiments with salt admixtures illustrating the data given in tables 15 and 16. The specimens containing 70.30 aniline—furfural resin appear favorably affected by several admixtures. However, this may in part be due to the fact that the control specimen for the respective batch had a strength of less than 100 lbs per sq in , whereas, for the majority of tests, the strength of the control specimens was about 200 lbs per sq in. Such check or control specimens were considered necessary for each batch because of the variation in the temperature and humidity at the time of preparation and curing, and of other known or unknown conditioning factors.

Sodium Silicate

Sodium silicate was investigated because of its possible cementing action and its possible catalyzing effect on the resin formation. Tables 11 and 12 give the results of these experiments and show that the effect of the sodium silicate is detrimental rather than beneficial

The Effect of Foaming Agents on the Quality of Two Aniline-Furfural Resins

Tables 17 and 18 show the effect of the addition of a combination of various foaming and gas producing agents. The proportion of gas-forming materials used for each specimen was calculated on the basis of a desirable pore pressure of 20 lbs per sq in. This appeared to be a suitable pressure, however, there is no way of predicting the optimum pressure for the purpose of concentrating the cementing resins on the points of contact of the soil particles.

None of the specimens showed any appreciable improvement, in fact some of them showed a decrease in strength from that of the control However, a beneficial effect could be observed from heating during the wet-dry tests

The Effectiveness of Two Percent Aniline-Furfural Resin (70 30) in the Stabilization of 10 Soils

The determination of the relative effectiveness of a stabilizing agent with widely different soils is a difficult task. No testing procedure has been developed that fully evaluates the properties of stabilized mixes employing resincus material, consequently, an analysis of laboratory results requires considerable knowledge of the general behavior of soils and an understanding of the forces of nature to which stabilized soils are subjected in the field

In this part of the investigation, the response of 10 different soils to stabilization with 2 percent aniline-furfural resin (70 30) was determined by two mechanical test procedures. first, by compressive strength tests on 2" x 2" specimens and, second, by plunger-penetration tests on 4^n x 6^n specimens. The data obtained from each of these tests are discussed separately

Compressive Strength - 2" x 2" Specimens

The results obtained from these tests are given in tables 19 to 28, inclusive Figure 9 shows the effectiveness of treatment as a function of the acidity or alkalinity of the media. Figure 10 is a plot of the strength of the treated soils after the different types of weathering. In this figure the soils are arranged from left to right in order of increasing plasticity. The discussion is divided according to the type of exposure to which the specimens were subjected.

Two-Fours Immersion Referring to figure 10, it is seen that immersing the specimens in water for 2 hours was not a sufficiently severe exposure to greatly affect the heavier soils N and V. Inasmuch as the specimens were air-dried before immersion and consequently were not all dried to an equal degree, and because unconfined tests show low stability for low-cohesive soils, the relative response of soils H, P, B, E, and L is difficult to determine. The comparatively high strength of soil G may or may not be an indication of success of treatment. This soil is probably better than soils U and M, however. No definite rating of the soils can be made from these data alone.

Alternate Wetting and Drying The graph showing the results of these tests presents an interesting factor about the reaction of the different treated soils to this type of weathering. It should be kept in mind that one wetting and drying cycle consisted of 5 hours immersion in water and 43 hours drying at an elevated temperature Because of the great water resistance of aniline-furfural treated specimens, little water was taken in curing the wetting period. As a consequence, these tests are more heating and cooling than wetting and drying tests

In will be noted that the strength of specimens of soils P, B, E, L and M was greater after 4-cycles than after 1-cycle, while that of soils H, G, U, N and V was less. The increase of strength of the first group of soils probably results from either or both the benefits of repeated drying during the cycling and/or the additional "set" of the resin at the elevated temperature used in drying. In the second group, the destructive forces exceeded any benefit that may have been gained. On the basis of this difference in performance and the relative strengths of the treated soils after 4 cycles of wetting and drying, it appears that soils P, B, E, L, G and U may be considered to have been satisfactorily treated. Although the latter two of these soils decreased in strength during cycling, they are included in this group because of their high strength after 4 cycles.

The effectiveness of treatment with soil H relative to the other soils is not shown by these tests since unconfined compression tests do not give a true comparison of the relative stability of cohesionless and plastic soils. The fact that this same was held together during the exposure shows that aniline-furfural resin has considerable birding power. It would seem, however, that a greater amount of treatment is required to satisfactorily stabilize this soil.

The data on soil M seem erratic — The only obvious peculiarity of this soil that might explain the large increase in strength during cycling is the activity of the clay fraction — The magnitude of this activity is shown by a high base exchange capacity

Scil A would be judged successfully stabilized soil if the specimen strength after 4 cycles were taken as the sole criterion of acceptability. The decrease in strength of tris soil during cycling indicates, however, that permanent stability has not been attained. An irrease in the amount of resin admixture would undoubtedly be advantageous.

The low strength of soil V after 4 cycles and the considerable reduction in strength during the cycle tests indicate that this soil was not satisfactorily treated with the 2 percent aumixture used

Alternate Freezing and Thawing Figure 10 shows that the freezing and thawing tests were considerably more severe or the specimens than the wetting and drying tests, especially in the case of the more plastic soils. This is an interesting item since plastic soils usually suffer less from freezing than non-plastic soils

While the strength of all specimens was quite low, a comparison of the response of the different soils to treatment is possible. Considering both the strength after 4 cycles and the reduction in strength during cycling, it seems that soil E should be judged the most susceptible to stabilization. Soil L, which on the basis of physical characteristics should perform quite similar to soil E, was much more affected by the weathering. As in the wetting and drying test, the strength of soil G was reduced

considerably during cycling but was still comparatively high at the completion of the test. Specimens of the sandy soils H and P were very resistant to freezing and thawing well. The action of soil V indicates that it was not sufficiently stabilized

Plunger-Penetration -- 4" x 6" Specimens

The main difference between a plunger-penetration type of test and a compressive strength test is the tendency of the former to measure the properties of a surface or outer crust of the specimens, proportional to the dimensions of the plunger, while the latter method tests the entire specimen. The relative merits of the two procedures are controversial, but, as far as this investigation is concerned, both provided pertinent data, and, in general, supported the same conclusions. The results obtained from the tests on the 4" x 6" specimens are given in table 29 and in figure 11

Capillary Absorption The original drying of the soils to a constant weight in an oven at 70° C reduced their moisture content from a range of 10-30 percent to a range of 1-3 percent, depending upon the soil type

After capillary absorption for 10 days the soils contained the following amounts of moisture, based upon the weight of the soil after drying in an oven at 70°C

H = 0.9%	G = 2.4%
P = 1.6%	U = 3.6%
B = 2.7%	M = 4.8%
E = 1.6%	N = 4.9%
L = 2.3%	V =•5 4%

These moisture contents are very low; therefore the load-penetration tests on these capillary absorption specimens was a measure of the properties of relative dry specimens. The low moisture contents indicate that the aniline-furfural resin was a very good waterproofing agent.

It is seen that the plunger-load sustained by all treated specimens after subjection to 10-days capillary absorption was considerable. The relative stability of the sandy specimens (soil H) is probably not truly reflected inasmuch as this test procedure provides no confinement for the specimen. The soils M and N were the most unstable.

Alternate Wetting and Drying The results of the alternate wetting and drying tests are given in the bar graph of figure 11. Besides showing the load sustained by the different soils after the cycling, the ratio of this load to that sustained after the capillary absorption test is given. Since the specimens used in these tests were exposed to the 10 days capillary absorption prior to cycling, the plot of this ratio of strengths provides an index of the effect of wetting and drying on the stability of the different soils

It may be seen that the strength of soils P, B, E, L, G and U was increased by the wetting and drying cycles, while that of soils H, M N, and V was decreased (ratio of the former is greater than one, - that of the latter is less than one). While, on the basis of load carried after cycling, soils L, U, and G appear the most stable, it will be noted that they were more greatly affected by wetting and drying than were soils P and B. A similar reversal of relationship is noted for soils M and V. The fact that soil N had, after the cycling, only 9 percent of the stability measured after the 10 days absorption period indicates that at least the surface of this soil was very detrimentally affected by the weathering cycles

The data obtained by the plunger and by the compressive strength test give the same general indications. The treated specimens of soils P, B, E, and L withstood wetting and drying exceptionally well. Soils G and U performed well but were not quite as well as the aforementioned group. Soils N and V were most affected by wetting and drying. The behavior of soil M is erratic, but it should be considered better than N and V though not as good as U. Judging from the test procedures employed, soil H requires more binder to withstand the cycling.

Alternate Freezing and Thawing. During the freezing and thawing cycles the specimens lost a small amount of moisture; consequently they were relatively dry at the time of the load-penetration test

Approximate moisture contents for the different soils after the freezing and thawing cycles are given below

H = O 4%	G = 2 2%
P = 0.5%	U = 4 0%
B = 2 8%	M = 4 1%
E = 1.5%	N = 6.7%
L = 2.5%	V = 5 0%

The results of the plunger tests performed after 12 cycles of freezing and thawing are given in figure 11, comparison being made between the load carried after exposure to freeze-thaw and the load after 10 days of capillary absorption. As in the case of the compressive strength tests, this type of exposure was the most severe employed. The general trends shown by both test procedures were the same. The less plastic soils resisted the exposure well while the heavier soils were considerably affected. The fact that soil L had, after the freeze-thaw exposures, only 44 percent of the load carrying capacity determined after capillary absorption shows that this soil differs greatly from soil E. The good resistance of soil H to freezing and thawing is of outstanding theoretical and practical significance.

The load-penetration values after 12 cycles of freezing and thawing were lower than those after 10 days*capillary absorption on all soils except E and M. This seems to indicate that the freezing and thawing cycles were destructive on most of the soils tested even though, at the low moisture contents prevailing in the specimens, there could be no question of a destructive action by ice formation

It appears that the effect of both the so-called wet-dry and freeze-thaw cycles was a result of the mechanical stresses caused by the temperature changes involved, and of the additional stresses caused by the differences in water affinity of the soils and the differences in the physical state of the absorbed water at the different temperatures involved in the cycle tests. 10

Summary

The test procedures employed in this study have not yet been correlated with observations on actual field installations using aniline-furfural resin as a stabilizer, therefore, no definite design criteria may be set at the present time. However, the tests do give a relative comparison of the response of the different soils to treatment with 2 percent of aniline-furfural. On the basis of the test results presented, the following summarizing comments may be made

- The fact that untreated specimens of all soils failed when immersed in water and treated specimens withstood even the most severe of the weathering tests indicates that aniline-furfural resin was beneficial in all cases
- The treated specimens of the medium plastic soils B, E, L, G, and U were very resistant to the alternate wetting and drying test Inasmuch as the destructive forces in these tests are due to the shrinkage and expansion of the specimens during changing moisture and thermal conditions, the successful treatment of these soils is probably due to their good gradation and low plasticity qualities that have been demonstrated as advantageous for all types of stabilization

¹⁰For greater detail concerning these phenomena see Winterkorn, Hans F, Climate and Fighways, Trans Am Geoph Union, June 1944.

- A comparison of the stability of soil N as measured by the compression tests and by the plunger test is of interest. In the former, this soil showed a relatively high strength while in the latter it made the poorest showing of all the soils. This may be explained by the fact that, in the first procedure of test, the properties of the entire specimens are measured while in the second, the properties of the outer crust or surface are evaluated. The presence of aniline-furfural in this specimen so reduced the water absorption that only the outer crust was affected during the period of exposure. The waterproofing of such a plastic soil demonstrates the effectiveness of this agent.
- The fact that all soils showed greater resistance to the wetting and drying exposure than to the freezing and thawing is quite significant especially since the destructive action involved could not be a consequence of ice formation, because of the low moisture content of the specimens. In general, stabilizing admixtures that owe their effectiveness to a binding or cementing property are more affected by the freeze-thaw test than by the wetdry test, for waterproofing admixtures, the reverse is true. This, of course, is a consequence of the use of cementing agents for noncohesive and of waterproofing agents for cohesive soils
- From the results obtained in this study it may be concluded that the effectiveness of aniline-furfural in the amounts employed is due mainly to its waterproofing properties
- That annline-furfural resin acts as a binding as well as a water-proofing agent is demonstrated in the resistance of the soil H specimen to freezing and thawing. Inasmuch as the test procedure employed is usually quite destructive on sardy soils, the relatively high strength of soil H is very significant.
- 7. The unexpected poor showing of soil L should serve as a warning of the danger involved in attempting to predict the response of a soil to treatment on the sole basis of its physical characteristics

Comparison of the Soil Stabilizing Effectiveness of Aniline-Furfural Resin (70 30) with that of Other Stabilizers

In order to compare the stabilizing effectiveness of aniline-furfural resin with that of other types of stabilizers, the results from a series of tests performed in another study are presented in tables 30 and 32. Because of the limited scope of these tests and the fact that laboratory tests do not always reflect the relative effectiveness in the field of different types of admixtures, the conclusions drawn are necessarily of a quantitative character. However, the results do demonstrate some interesting properties of aniline-furfural resin

Table 32 shows the results obtained from a series of tests employing portland cement, a liquid asphalt, and aniline-furfural resin with six different soils 11. The characteristics of these soils are given in table 31. The plunger test, as previously described, was used in this study

llThese tests were performed by the Joint Highway Research Project, Purdue University, as part of a project on soil stabilization sponsored by the Civil Aeronautics Administration

Since the effectiveness of portland cement with soils is due to its binding properties and that of liquid asphalt to its waterproofing properties (excluding granular mixes and asphaltic cements), the effectiveness of aniline-furfural resin can perhaps best be seen by comparing the strength of the specimens containing this agent with those made with portland cement, and the moisture absorption with those containing the liquid asphalt. Following this procedure, it may be seen that the aniline-furfural resin compares favorably with cement in binding properties and, at the same time, performs as well as liquid asphalt in waterproofing the soils

Table 30 presents a comparison of the effectiveness of aniline-furfural resin, a purely waterproofing type of agent designated as Resin Stabilizer 321, and portland cement. It may be seen that by the procedure of test employed (compressive strength of 2" x 2" specimens), aniline-furfural resin appears to be a very effective stabilizer. Inasmuch as Resin 321 has been shown to be very effective in waterproofing the soils in question, 12 the binding properties of the aniline-furfural resin probably account for the differences in strength obtained. It is interesting to note that soils treated with Resin 321 showed practically no stability after the freezing and thawing test — an indication that Resin 321 has no binding effect. A comparison of the strengths of the aniline-furfural specimens and the cement specimens after wetting and drying again demonstrates the excellent waterproofing properties of this resin

TEST RESULTS II - OTHER ARTIFICIAL RESINS

The Effectiveness of Urea-Furfural and Phenol-Furfural Resins 13

The results of the experiments on urea-furfural and phenol-furfural resin binders are given in tables 34 and 36, respectively. The phenol-furfural resins did very poorly even with aniline-furfural admixtures. The urea-furfural results were more encouraging but still not nearly as good as those achieved with aniline-furfural. In later experiments urea-furfural was used in combination with natural resin stabilizers Table 35 shows the effectiveness of urea-furfural with Belro Rosin in the stabilization of soil G. Experiments using Belro Rosin as a stabilizing agent and urea (from urine) and furfural as dispersing agents were performed with soil N. The results of these tests, however, were very poor. Evidently, as in the case of many other resins, urea-furfural resins cannot be used effectively in heavy clay soils at the low densities employed in this test series.

The Effectiveness of Phenol-Formaldehyde Combinations

Combinations of phenol and formaldehyde were tried on Nimitz fine sand (soil H) The specimens failed upon contact with water, showing that the material did not set at the low temperature employed.

¹²McAlpin, George W , Mainfort, Robert C , and Winterkorn, Hans F , "A Laboratory Study of the Soil Stabilizing Effectiveness of a Complex Salt of Abietic Acid " CAA Technical Development Note No 35

¹³The effectiveness of these and of other artificial resins depends, of course, to a great extent upon the method of preparation of the resins and of the soil-resin specimens. In this study, such methods of preparation were selected as could be easily adapted to prevailing construction methods. It follows that the conclusions drawn here hold only for the stated experimental conditions and for comparable field methods and conditions.

The Effectiveness of Urea-Formaldehyde Resins

Tables 37 to 39 show the results of experiments using urea-formaldehyde resing including a commercial brand named "Weldwood glue" Though several salt catalysts were used, nowhere in these experiments was a direct acid-base catalysis attempted. In those experiments in which acid forming salt were used the PH value of the treated soil was not recorded. It should also be noted that for the experiments recorded in table 38 amounts of resin only slightly greater than 1 percent were employed, even the very effective aniline-furfural resins showed poor strength at the prevailing low soil densities until quantities of 2 percent or greater were used.

Olmstead and Klipp¹⁴ found greater percentages (4 percent) of dimethylol urea effective in soil stabilization; however, they used a DuPont preparation, while our stabilizer was prepared in the laboratory from urea and formaldehyde. They also made use of acid catalysts just before the addition of the resin to the soil

The field for the development of this resin is still open. Better results could, possibly, be achieved by adding the acid catalyst to the soil just previous to the addition of the dimethylolurea. Also some of the difficulties encountered by Olmstead and Klipp might be overcome by keeping the resin solution alkaline until it is added to the acidified soil

The effectiveness of Calcium Sulfamate-Formaldehyde Resins

Table 40 gives the results obtained by the use of calcium sulfamate-formalde-hyde resins. These results do not appear to be very good. However, very little work has been done on this material and it might well bear further investigation especially since the water insoluble resin is easily formed by an exothermic reaction.

The Effectiveress of Aniline-Furfural Resins in Conjunction with Vinsol, Congo Resins, and Semi-Solid Amires

Table 41 shows the effectiveness of aniline-furfural resin in conjunction with Congo resins and Vinsol Two percent of resinous material were used in each batch one percent of Vinsol or of the particular Congo resin and one percent of 70 30 aniline-furfural resin The resin mixture was prepared by dissolving the Congo resir or Vinsol in the furfural, then adding the mixing water and aniline to the furfural solution and emulsifying the mixture in a milk shaker before adding it to the soil. The results, given in table 41, show that none of the resin mixtures proved to give as good results as the 2 percent aniline-furfural resin control sample on any of the 4 soils tested

Specimens were made using a 2 percent of aniline-furfural resin (25 75) in conjunction with two semi-solid amines. Four and one-half percent of amine (on the basis of resin added) was combined with the ariline-furfural solution, and the resulting solution mixed with the soil. The results showed no improvement over the control of 2 percent aniline-furfural resin and are not recorded in this report.

CONCLUSIONS

On the basis of the experiments performed in this investigation, the following conclusions may be stated

1. Two appline-furfural combinations were found which gave reasonably good resin binders. These represented ratios of 70 30 and 35.65 of aniline and furfural, respectively. The 70 30 resin was much stronger and withstood weathering tests far better than the 35.65 resin.

¹⁴⁰¹mstead, Lewis 8 and Klipp, L W "Chemical Soil Stabilization of Soils for Military Uses," Research Report No 22

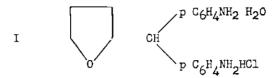
- Both resins mentioned above were found to give poor results in alkaline mixes Maximum strengths were obtained when the mixes were slightly on the acid side
- A minimum of approximately 2 percent of the best anilinefurfural resin (70 30) was required to obtain appreciable resistance to weathering for the low specimen densities employed
- 4 The addition of iron or aluminum salts was found to improve slightly the strength of the resin while the addition of alkaline reacting materials was found to be detrimental
- Foaming agents combined with gas producing materials were found unsuccessful in improving the strength of the specimens
- Annline-furfural resin (70 30) is most effective with medium plastic soils. Cohesionless soils and heavy clays probably require greater amounts of admixture for successful treatment, however, the amount required also depends upon the compacted densities of the soil.
- 7 Aniline-furfural resin is both a binding and a waterproofing agent both properties are of considerable significance with quantities of admixtures as small as 2 percent
- 8 Urea-furfural, phenol-furfural, and phenol-formaldehyde resins were found ineffective as soil stabilizing agents in the amounts and form used
- 9 Urea-formaldehyde and calcium sulfamate-formaldehyde specimens showed some promise but the experiments performed were not conclusive

APPENDIX I

THE HISTORY AND STRUCTURE OF ANILINE-FURFURAL RESINS

The formation of resinous masses by reaction of furfural with various substances has been known for a long time. Such materials were produced by $Persoz^{15}$ in 1860 and Stenhouse¹⁶ in 1870 from furfural and aromatic amines or phenols. However, no concise report was made at that time on either the reaction mechanism or the reaction products

 $Schiff^{17}$ in 1870 assigned the formula



to the product obtained by the reaction of 1 mole of furfural with 1 mole of aniline and 1 mole of aniline hydrochloride. He considered the compound to be a derivative of furyl diphenyl methane possessing a structure analogous to the dye stuffs of the triphenyl methane class

Zincke and Mulhausen¹⁸ in 1905 concluded that the furfural ring opened up in the reaction giving the open chain compound

Riegel and Hathaway¹⁹ (1941) titrated the product with nitrous acid and found that it reacted quantitatively. From this formation of the diazonium salt they concluded that the structure must be as shown in Formula I in order to permit the free NH₂ groups fo be diazotized.

However, Williams and Wilson²⁰ discovered (1942) that in the formation of the diazonium salt of Riegel and Hathaway aniline is liberated. They also found that treatment with NaHSO₃ liberated aniline from the aniline-furfural product. Though the fate of the remainder of the molecule is unknown because of the ease of splitting off aniline from the open chain compound compared to the difficulty that supposedly would be encountered in aplitting off aniline from the dianilinofuryl methane structure, the authors concluded that the correct structure is that proposed by Zincke and Muhlhausen, Formula II. They also indicated that the dianilinofuryl methane structure could not give the

¹⁵ Persoz, Wagner's Jahres Berichts, p.487, (1860)

¹⁶ Stenhouse, <u>Proc Roy Soc.</u>, Vol 18, p. 537 (1870) <u>Ann</u>, pp 156, 199, (1870)

¹⁷ Schiff, Ann , pp. 201, 355, (1880) Ann , pp 239, 349, (1887)

¹⁸ Zincke and Mulhausen, Ber., Vol 38, pp 382-1, (1905)

¹⁹ Riegel and Hathaway, J Am Chem Soc, Vol 63, p 1835 (1941)

²⁰ Williams and Wilson, J. Chem. Soc., pp. 506-7, (1942)

deep reddish blue color found in the aniline-furfural product which the open chain structure very easily explains

Compounds of the Formula II type are known to crystallize easily, while the free bases generally appear as resinous masses. Since the investigation described in this report was concerned with a <u>resin</u> stabilizer, the work was done using 2 moles of aniline to combine with 1 mole of furfural instead of the usual combination using 1 mole of aniline and 1 mole of aniline hydrochloride

For the purpose of checking the proposed structural formulas, two sets of experiments were performed using p-toluidine and dimethyl aniline respectively, instead of aniline. In the case of p-toluidine the proposed of the benzene ring is full and the reaction should not go if Formula I is the structural formula. Structural formula II requires the amino group to be free and theoretically p-toluidine would make a resin under this proposed structure. The case of dimethyl aniline is just the reverse. A resin would not be formed if II is the correct formula, while, since the proposition is open the resin would be formed according to I

Specimens 2 inches high and 2 inches in diameter were compacted from Nimitz fine same (soil H) containing 2 percent aniline-furfural in the first 3 batches, 2 percent dimethyl aniline furfural in the next 3 and 2 percent p-toluidine furfural in the last batches. These samples were then subjected to the regular freeze-thaw and wet-dry tests. The results are shown in table 33

It can easily be seen that the dimethyl aniline furfural specimens did not stand up at all, indicating there was no resin formed. On the other hand, while the p-toluidine furfural specimens did not stand up as well as the aniline-furfural specimens, they did far better than the dimethyl aniline furfural. These results lend support to Formula II

The series of tests made to find the best proportions of aniline and furfural for resin formation brought out two maxima in the curve (figure 2). The first and most pronounced coincided with the ratio of 1 mole of furfural to 2 moles of aniline. The corresponding molecular structure has already been discussed. The second maximum coincides with the ratio of 2 moles of furfural to 1 mole of aniline. The structure of this reaction product is probably.

This formula is analogous to that for the condensation product of phenols and aldehydes. However, at present, the data available are too scarce to permit a definite decision whether the material obtained is a chemical compound or a mixture of 2 laniline-furfural resin with furfural and spontaneously formed furfural resins

The resinous material thus formed is not as effective a stabilizer as the 2.1 annline-furfural compound

APPENDIX II

ANILINE-FURFURAL RESIN CATALYZATION

Recent work with aniline-furfural has shown a retardation of the condensation reaction which with the technical grades of these materials available 10 years ago, started spontaneously and instantaneously, immediately upon combination. This fact represents an advantage insofar as it permits a better control of the reaction. However, for the latter purpose it is important to have the right catalyst available. The tests described in the following were made in an attempt to discover and evaluate an effective and adjustable catalyst for the aniline-furfural reaction. These tests were concerned with

- 1 The Effectiveness of Powdered Chemicals as Catalysts
- 2 The Catalytic Effectiveness of Aqueous Salt Solutions
- 3 The Effect of Increasing Amounts of Water on Resin Formation
- 4 Annline-Furfural Emulsions

The Catalytic Effectiveness of Powdered Chemicals

Batches containing 2 parts, by weight, of aniline to 1 part of furfural, making a total of about 21 cc of the mixture, were prepared with small amounts of potential catalysts. A duplicate was made for each test with the addition of 2 cc of water

One sample containing only aniline and furfural was set aside as a control This sample was still soft after standing 3 days. The sample containing 2 cc of water (no catalyst) behaved the same way

The addition of a slight amount of ferric chloride produced solidification both with and without water, but produced better results without water. Possibly a little more of the ferric salt was added to the sample without water

Ferric sulphate produced a solidification, but to a very much lesser degree than the chloride, and the solidification was not noticeable until several days after adding the catalyst

The addition of aluminum chloride caused thickening in the sample containing water in about 30 minutes. In the sample without water the reaction was slower, but still definite

Barrum chloride, sodium chloride, lead chloride, and calcium sulphate were tried but produced no thickening or hardening effect on the mixture. The addition of small amounts of phosphoric acid produced a precipitate which appeared to be an aniline phosphate instead of the resin desired.

This group of tests (table 42) pointed at the iron and aluminum chlorides as the best catalysts for the purpose. As a check test, two samples were prepared in the same manner as above, one with water and one without water, adding a very small amount of aluminum chloride to each. In one additional sample with the aluminum chloride, I drop of phosphoric acid was added causing a slight precipitate as noticed in the earlier tests. All samples showed thickening, but not very good solidification

The Catalytic Effectiveness of Aqueous Salt Solutions

From these preliminary tests, the question arose as to the amount and form in which the iron or aluminum chloride would be most effective. Therefore, tests were made using different amounts of these salts in aqueous solution. The resins were made as formerly. Ten grams of aluminum chloride (6 H₂O) were dissolved in 25 cc of water;

and 10 grams of ferric chloride (6 H₂0) were dissolved in 20 cc of water. All tests were made on the pure aniline-furfural mixture without any water except that contained in the catalyzing solution.

To identical samples of the aniline-furfural mixture were added 1/2 cc, 1 cc, 2 cc, 3 cc, 4 cc, and 5 drops (1/4 cc) of catalytic solutions (table 43). All samples became hard after a day and a half. In general it was observed that the greater the amount of the catalyst added, the more rapid the reaction. When 3 or 4 cc were added, the mixture hardened before the catalyst could be thoroughly stirred into the batch. The samples containing 1 cc of the catalyst became thick fairly soon after the addition of the catalyst, but did not harden for 4 or 5 hours. The samples in which 5 drops of catalyzing material were added took over night to harden. The aluminum chloride produced a better effect for the amount added than the ferric chloride. Much better results were shown when the catalyst was added in solution than when it was added in the crystal form

The Effect of Increasing Amounts of Water on Resin Formation

In order to determine whether or not the action of these catalysts was appreciably affected by the presence of larger quantities of water, batches of the resin were made in the same manner as before, adding increasing amounts of water. Six samples were used with each catalyst, a control, in which no water was added, and 5 other samples, to which increasing amounts of water were added. To the first six samples 5 drops of ferric chloride solution were added to each batch, to the second six, 5 drops of aluminum chloride solution (table 44). The samples were stirred well in an attempt to disperse the water into the aniline-furfural mixture. However, these attempts were not very successful. With one sample an attempt was made to emulsify the aniline-furfural solution and the water. However, the emulsifier became clogged, and this process had to be discontinued, however, such emulsification was carried out at a later date in other experiments. In these experiments the water remained in a separate phase from the aniline-furfural solution, and had no effect on the solidification of the resin

Aniline-Furfural Emulsions

Batches of aniline and furfural were made using 13 7 cc of aniline and 6 7 cc of furfural in each batch. Five drops of ferric-chloride solution (10 grams of ferric chloride in 20 cc of water) were added to each batch (table 46). The first batch was used as a control. To succeeding batches, increasing amounts of water were added. All samples were emulsified with ferric chloride added at the time of emulsification. Probably the catalyst was not well dispersed in the control sample, a large dark red spot remained in the emulsifier after the emulsification had been completed

After 1 hour the control sample had developed into a soft resin, the sample containing 5 cc of water had become a viscous liquid; the sample containing 10 cc of water seemed to have a surface scum thicker than the main body. The other samples appeared unchanged

After 2 hours apparently all the emulsions held except the sample containing 25 cc of water The emulsion had been broken in that case, and the aniline-furfural mixture had settled to the bottom.

The next observation was made after 3-1/2 hours The control was still soft resin. The samples containing 15, 20 and 25 cc of water had broken from the emulsion, and, instead of forming a brittle-like resin, as is usually the case with aniline-fur-fural, they formed a more or less flocculent precipitate. This tendency to form a flocculent precipitate appeared to be more prevalent as more water was added. The sample containing 10 cc of water was gummy and showed tendencies to be flocculent. In the 5 cc sample, after the soft resin formed, the water collected in the center and there was a tendency to show a fluffy nature in this aqueous portion.

In a second group of experiments, batches of aniline-furfural were made in the same manner, except that alumnum chloride solution (10 g in 25 cc water) was added in place of ferric chloride.

The control formed quite a hard resin immediately upon emulsification with the catalyst. The second sample, having 5 cc of water, formed a viscous resin from which water could be squeezed showing that the emulsion was not badly broken before the resin set. However, the resin formed was very soft. The sample containing 10 cc of water formed a flocculent precipitate on the bottom of the cup with a gummy resin on top. The emulsion in all samples having more than 5 cc of water were not stable, but broke before or during the reaction; the aniline-furfural settling to the bottom of the cup and the water standing over it

It was found difficult to emulsify the mixture when the catalyst was added at the time of emulsification because chunks of resin would stop up the emulsifier. Therefore a series of experiments was made in which the amiline-furfural and water were emulsified and the catalyst added later. It was also desired to see the effect of larger amounts of water; therefore, to 400 cc of water were added 13 7 cc of amiline, 6.7 cc of furfural and 5 drops of respective catalytic solutions. Samples were prepared in which the catalyst was added both before and after emulsification (table 45).

In the cases where the catalyst was not added until after emulsification, the emulsified liquid came out white and milky in color. Upon the addition of 5 drops of the catalyst, the aluminum chloride sample turned pink, and a thick flocculent precipitate was formed. Upon the addition of the ferric chloride catalyst to another sample of the same emulsion, the solution turned a dark brown, and a small precipitate was formed. A check test turned out the same as the original

Samples of the emulsion were taken and the amount of the catalyst was tripled The effect was that a thicker and more strongly colored precipitate was formed more quickly in both cases with the aluminum chloride showing the best over-all flocculent effect. The brown color when the iron catalyst was used, and the red color when the aluminum catalyst was used, may indicate that the flocculent precipitates which were obtained were not true aniline-furfural resins, but aluminum and iron complex compounds.

It was found that the emulsification of the aniline-furfural and water in an aluminum emulsifier caused the reaction to be catalyzed sometimes to the extent that a flocculent precipitate was formed. However, it was found that a stable emulsion could be obtained by adding a small amount of soap to keep the mixture on the alkaline side until the catalyst was added.

Conclusions

- 1. The best catalyst found for the aniline-furfural reaction was AlCl3 It was most effective when added as a saturated, or nearly saturated, aqueous solution
- 2. FeCl₃ was not quite as effective as AlCl₃ It was more effective when added as a saturated, or nearly saturated, solution than when added in powder form
- 3 The greater the amount of either of these catalysts used, the greater was the acceleration of the reaction (5 percent AlCl₃ added as a saturated aqueous solution produced solidification before the catalyst could be thoroughly mixed with the 21 cc of aniline-furfural used)
- 4 BaCl2, FeSO4, NaCl, PbO, and H3PO4 were tried as catalytic agents, but did not produce good results
- 5 FeSO4 catalyzed the reaction, but much more slowly than either FeCl3 or AlCl3
- 6. H3PO4 produced an aniline phosphate precipitate.
- 7 The presence of large quantities of water was found to decrease the effectiveness of the catalysts. A soft, gummy resin was formed which tended to settle out at the bottom in tests in which the water was just stirred into the aniline-furfural mixture. However, if the water was emulsified with the aniline-furfural mixture, the resin formed as a flocculent precipitate.
- 8 In cases where the samples were emulsified, it was found to be more practical to add the catalyst after the material had been emulsified.
- 9 The addition of a small amount of soap was effective in keeping the reaction from taking place in the aluminum emulsifier

TABLE 1

PHYSICAL CHEMICAL CHARACTERISTICS OF THE TEN SOILS EMPLOYED IN THE INVESTIGATION

Soil	Colloia %	radat; Clay		Sand	Atte L L	rburg P L	Limits P I	S L	Organic Matter %	Base Ex Capacity (1)	Optimum Max Moisture % (2)	Dry Density Lbs/Cu Ft (3)
H	4	5	5	90	No	n Plas	stic		0 42	2 17	12	103
P	9	11	1.2	77	19 0	17 0	2 0		1 00	5 62	14	109
B	1,4	22	11_	67	22 1	18 1	4 0	14 4	1 36	9 28	14 5	113 5
E	14	18	32	50	22 5	18 3	4 2	15 3	2 47	8 84	14	115
L	9	17	28	55	23 C	18 C	5 0	16 3	1 47	8 71	14 C	101 3
G	7	17	53	30	25 0	18 6	6 4	15 6	1 38	12 86	15	110
U (3)	12	20	4-	39	31 8	20 1	11 7	14 9	1 32	10 15	16	110
<u>I</u> v	12	25	30	45	32 1	18 4	13 7	15 6	1 79	16 24	17	104
N	19	40	27	33	45 0	19.0	26 C	12 6	1 95	13 59	22	96
V	20	45	21	34	53 5	22 4	31 l	12 7	3 02	18 48	28	90

⁽¹⁾ Multi-equivalents per 100 g (2) By modified procedure described in text (3) This soil contains free ${\rm CaCO}_3$

TABLE 2

THE EFFECT OF THE ANILINE-FURFURAL RATIO ON THE QUALITY
OF THE RESINOUS CEMENT (NO CATALYST)

Anılıne - Ra	Com	Compressive Strength in Lbs/Sq In						
Anılıne %	Furfural %	Dry	Wet	Dry 1 W-D	Wet 4 W-D	Moist 1 F-T	Wet 4 F-T	
10	90	84	26	85	34	25	10	
20	80	79	33	59	29	25	27	
30	70	125	39	92	32	35	30	
40	60	167	40	121	38	40	33	
50	50	134	50	158	31	34	35	
60	40	262	148	153	49	67	72	
70	30	450	239	271	70	144	132	
8 0	20	221	150	108	26	50	21	
90	10	98	25	69	29	23	8	
0	100	58	6	70	6	12	*	

^{*} Mechanical defect
Batch Composition Soil H, 2% Aniline-Furfural
Mixture, no catalyst

•

TABLE 3

THE EFFECT OF THE ANILINE-FURFURAL RATIO ON THE QUALITY OF THE RESINCUS CEMENT IN THE PRESENCE OF O 08% HCl AS CATALYST

	Aniline - Furfural Ratio		Compressive Strength in Lbs/Sq In						
Aniline %	Furfural	Dry	Wet	Dr y 1 W -D	Wet 4 W⊸D	Moist 1 F-T	Wet 4 F-T		
10 20 30 40 50 60 70 60 90	90 80 70 60 50 40 30 20 10	40 46 60 43 58 289 207 225 16	10 14 16 8 62 147 128 40 5	*** 11 19 29 80 67 41 8	10 13 12 10 14 40 11 28	5 8 9 ** 3 55 75 11 5 **	4 9 8 4 10 52 46 13 5 **		

-∹ Failed

Batch Composition Soil H, 2% Annline-Furfural Mixture, 0 08% (1 1/2 cc) HC1

TABLE 4

THE EFFECT OF THE AMILINE-FURFURAL RATIO OF THE RESIDOUS CELENT IN THE PRESENCE OF O 16% HOL AS CATALYST

1	Anılıne — Furfural Ratıo			Compressive Strength in Lbs/Sq In						
Anılını %	Furfural	Dry	Wet	Dry 1 W-D	Wet 4 W-D	Moist 1 F-T	Wet 4 F-T			
10 20 30 40 50 60 70 80 90	90 80 70 60 50 40 30 20 10	37 78 137 188 136 116 136 81 48 57	24 45 95 109 123 99 75 26 22	38 88 131 182 137 110 80 45 35	7 17 29 41 34 31 23 16 9	21 33 61 73 61 58 41 26 17	9 26 38 37 29 35 31 12 8			

** Falled

Batch Corposition Soil H, 2% Aniline-Furfural Mixture, 0 16% (3 cc) HCl

TABLE 5

THE EFFECT OF THE ANILINE-FURFURAL RATIO OF THE QUALITY OF THE RESINOUS CEMENT IN THE PRESENCE OF O 05% NaOH AS CATALYST

Aniline — Furfural Ratio			Com	press	ve Str	ength 1	n Lbs/S	q In
	Anılıne %	Furfural %	Dry	Wet	Dry 1 W-D	Wet 4 W-D	Moist 1 F-T	Wet 4 F-T
	10 20 30 40 50 60 70 80	90 80 70 60 50 40 30 20	83 84 130 122 86 177 217 201 94	** ** ** ** 9 22 18 12	** ** ** ** 212 154 96	** ** ** 24 25 17	*** ** ** 7 13 10 4	* * * * * * 5 5 8
	Ō	100	92	**	**	**	#-¥	**

** Failed

Batch Composition Soil H, 2% Annline-Furfural Mixture, 10% (10 cc) NaOH

TABLE 6

THE EFFECT OF ITOROGEN AND HYDROXYL IONS (FROM HC1 AND NaOH)
ON A 50 50 ANILINE-FURFURAL RESIN

Catalyst		mpress	ıve Stre	ength in	Lbs/Sq	 In
cc	Dry	Wet	Dry	Wet	Moist	Wet
			1 W-D	4 W-D	1 F-T	4 F-T
Conc HCl]		
0.5	98	10	33	28	23	4
10	81	7	40	22	21	13
15	147	13	31] 16	18	15
20	74	14	44	18	10	12
3.0	119	37	29	20	7	23
None	39	**	29	15	**	2
10% NaOH						
1	38	2	74	28	3 -≍	1
2	51	* *	68	19	**	* *
4	85	**	45	24	**	¥¥
6	84	**	**	**	**	**
8	106	**	**	∦×	* -⊁-	× ⊀
10	105	**	*-×	⊹ .×	××	አ ጉ
L		<u> </u>	<u> </u>	<u></u>	L	

* Failed

Batch Composition Soil H, 2% Annline-Furfural Resin (50 50) Amounts of catalyst shown were added to 2200 g of soil

TABLE 7

THE EFFECT OF HYDROGEN AND HYDROXYL IONS (FROM HC1 AND NaOH)
ON A 35 65 ANILINE-FURFURAL RESIN

Catalyst	Co	mpress		ength in	Lbs/Sq]	 [n
cc	Dry	Wet	Dry	Wet	Moist	Wet
			1 W-D	4 W-D	1 F-T	4 F-T
Conc HCl						
0.5	66	43	37	26	26	91
10	67	67	47	23	51	34
20	62	32	26	26	35	34 14
3 0	64	20	34	26	17	13
None	43	11	20	22	9	9 '
10% NaOH			_			
1.0	63	13	63	36	13	10
20	86	16	54	19	13	11
4.0	8 9	5	71	25	5	[6]
6.0	82	其 关	₩ж	+6->∸	**	≯ *
8 0	118	-} - -/-	**	 ≭ *	*~	¾ ⊬
10 0	. 88	**	**	**	**	**
<u> </u>				L		

** Failed

Batch Composition Soil H, 2% Aniline-Furfural Resin (35 65). Amounts of catalyst shown were added to 2200 g of soil

TABLE 8

THE EFFECT OF HYDROGEN AND HYDROXYL IONS (FROM HC1 AND NaCH)
ON A 70 30 ANILINE-FURBURAL RESIN

Catalyst	Co	mpress	ıve Stre	ngth in	Lbs/Sq 1	.n
cc	Dry	Wet	Dry 1 W-D	Wet 4 W-D	Moist 1 F-T	Wet 4 F-T
Conc HCl 0 5 1 0 2 0 3 0 None	481 317 119 118 395	230 113 89 78 207	96 62 28 95 95	65 51 31 20 71	9 2 51 32 31 90	62 31 37 19 82
10% NaOH 1 0 2 0 4 0 6 0 8 0 10 0	321 209 286 272 341 401	86 100 32 19 14 62	66 44 62 75 49 52	29 38 55 63 54 44	50 32 15 13 11 23	40 17 10 6 9

** Failed

Batch Composition Soil H, 2% Aniline-Furfural Resin (70 30) Amounts of catalyst shown were added to 2200 g of soil

TABLE 9

TIE EFFECTIVENESS OF LOW PERCENTAGES OF 70 30 ANILINE-FURFURAL RESIN IN ACID, ALKALINE, AND NEUTRAL MEDIA

Percent	Catalyst	Com	press:	ıve Str	ength 1	n Lbs/S	q In
Resin	cc	Dry	Wet	Wet 1 W-D	Wet 4 W-D	Wet 1 F-T	Wet 4 F-T
0 5 1.0 1 5	None None None	72 157 291	33 96 161	17 30 64 76	14 26 17	17 30 76	10 23 52
2 0	None HCl.	420	303	'76	64	121	104
0.5 1 0 1 5 2 0	0 75 1 50 2 30 3.00	53 56 54 124	22 26 36 57	10 11 11 20	14 12 14 37	7 9 15 32	6 8 13 28
0 5 1.0 1 5 2 0	10% NaC 2 5 5 0 7 5 10 0	149 232 304 393	56 25 22 12	19 30 15 44	38 55 60 63	19 13 10 9	16 9 6 6

TABLE 10

THE EFFECTIVENESS OF LOW PERCENTAGES OF 35 65 ANILINE-FURFURAL RESIN IN NEUTRAL MEDIA

Percent		Compressive Strength in Lbs/Sq In								
Resin	Dry	Wet	Wet 1 W-D	Wet 4 W-D	Wet 1 F-T	Wet 4 F-T				
1 2 4	93 64 3 2	9 10 14	18 14 55	8 5 24	14 15 16	12 7 12				

Patch Composition
Resin (35 65)
Soil H, Aniline-Furfural

TABLE 11

THE EFFECT OF VARIOUS IONS ON THE QUALITY
OF 35 65 ANILINE-FURFURAL RESIN

	Co	mpres	sive St	rength :	in Lbs/	Sq In
Catalyst	Dry	Wet	Wet	Wet	Wet	Wet
			l W-D	4 W-D	1 F-T	4 F-T
None (Control)	200	135	71	34	88	57
		Catio	n Effec	t	_ 	
ll g NaOH	155	**	22	25	*-~	**
l 15 g KCH	71	9	26	22	2	5)
2 2 g BaOH	67	12	28	14	9	7 (
0 7 g Ca(OH) ₂	76	13	28	16	8	8
		Аплоп	Effect			
13 g H ₂ SO ₄	160	106	70	38	50	51
17 g HAc	186	135	5 5	51	53	63
2 25 g HNO ₃	173	104	95	36	74	66
08 g H ₃ PO ₄	162	171	88	25	87	65
	Effect					
10 cc 50% Na2S1409	86	14	27	22	10	7
10 cc 50% Na ₂ S1 ₄ 0 ₉ 20 cc 50% Na ₂ S1 ₄ 0 ₉	123	45	61	33	28	20

Failed

<u>Batch Composition</u> Soil H, 2% Amiline-Furfural Resin

(35 65) Amounts of catalyst shown were added to 2200 g

of soil

TABLE 12

THE EFFECT OF VARIOUS IONS ON THE QUALITY
OF 70 30 ANILINE-FURFURAL RESIN

	Çc	mpres	sive St	rength:	ın Lbs/	Sq In
Catalyst	Dry	Wet	Wet	Wet	Wet	Wet
			1 W-D	4 W-D	1 F-T	4 F-T
		Cation	n Effec	:t		
ll g NaOH	117	8	32	26	**	**
1 15 g KOH	232	19	135	53	12	6
43 g Ba(OH) ₂	38	7	60	41.	8	5 B
$2.2 \text{ g Ba}(0\text{H})_{2}^{2}$	124	13	2 9	28	11	
14 g Ca(OH)	148	20	27	37	14	1.2
0 7 g Ca(OH)2	131	16	36	38	14	5
		Anion	Effect	5 <u> </u>		
11 g H ₂ SO ₄	544	271	98	67	121	66
17 g HAC	272		52	55	61	32
2 25 g HNO ₃	255	139	58	43	70	7⊥
08 g H ₃ PÓ ₄	446	199	84	69	101	55
	Effect					
10cc 50% Na ₂ 51409	192	21	41	51	16	6
10cc 50% Na ₂ 51 ₄ 0 ₉ 20cc 50% Na ₂ 51 ₄ 0 ₉	1081	10	**	** 	7	#*X

** Failed

Batch Composition | Soil H, 2% Aniline-Furfural Resin (70 30) | Amounts of catalyst shown were added to 2200 g of soil

TABLE 13

THE EFFECT OF INCREASING AMOUNTS OF SULFURIC ACID ON THE QUALITY OF 35 65 ANILINE-FURFURAL RESIN

H ₂ SO ₄	Dry	Compr Wet	essive Str Wet l W-D	ength in . Wet 4 W-D	Lbs/Sq In Wet 1 F-T	Wet 4 F-T
1 4	127	138	77	30	57	35
2.8	204	162	75	**	61	43
5 6	162	160	72	**	46	44
8 4	219	163	94	32	49	64
11 2	120	78	80	27	48	30
14 0	131	106	65	39	59	44

** Failed

Batch Composition Soil H, 2% Annline-Furfural Resin (35 65) Amounts of catalyst shown were added to 2200 g of soil

TABLE 14

THE EFFECT OF INCREASING AMOUNTS OF SULFURIC ACID ON THE QUALITY OF 70 30 ANILINE-FURFURAL RESIN

H ₂ SO ₄	Dry	Compr Wet	Compressive Strength in Lbs/Sq In Wet Wet Wet Wet 1 W-D 4 W-D 1 F-T					
1 4	418	168	85	44	106	85		
2.8	314	204	77	37	95	60		
5 6	402	229	96	55	116	109		
8 4	246	172	68	33	84	95		
11 2	340	145	77	40	82	73		
14 0	250	131	85	37	71	63		

Batch Composition | Soil H, 2% Aniline-Furfural Resin (70 30) | Amounts of catalyst shown were added to 2200 g of soil

TABLE 15

THE EFFECT OF VARIOUS SALTS ON THE QUALITY
OF 35 65 ANILINE-FURFURAL RESIN

	Compre	951V6	Stre	ngth in	Lbs/S	5q In
Catalyst	Dry	Wet	Wet	Wet	Wet	Wet
			l W-D	4 W-D	1 F-T	4 F-T
None	158	131	25	21	12	7
6 3 g Fe ₂ (50 ₄) ₃ 6 H ₂ 0	109	113	74	35	25	27
3 2 g Fe ₂ (SO ₂) 6 H ₂ O	124	93	66	26	27	10
2 3 g FeCl ₃ . 6 H ₂ D	143	76	57	21	34	29
20g AlCl ₃ 6 H ₂ 0	206	116	22	35	49	59
20g ZnSO ₄ 7 H ₂ 0	168	97	81	22	29	26
3 0 g MgSOZ H2O	132	49	33	13	21	7
5 4 g Al ₂ (SO ₄) ₃ 18 H ₂ O	129	149	68	38	66	40
5 7 g Al2(SO4)3(NH4)2SO4	128	109	47	41	56	45
24 H ₂ 0						
3 5 g Na ₂ HPO ₄	134	10	23	10	-4*	*#

Batch Composition Soil H, 2% Anıline-Furfural Resin (35 65) Approximately 1/40 mole of salt shown

TABLE 16

THE EFFECT OF VARIOUS SALTS ON THE QUALITY OF 70 30 ANILINE-FURFURAL RESIN

	Compre					eq In
Salt g	Dry	Wet	Wet	Wet 4 W—D	Wet ≀ F_T	Wet √F_T
			- 11-2	4 **		
None	221	67	58	43	119	20
6 3 g Fe ₂ (SO ₄) ₃ 6 F ₂ O	37	21	15	15	14	18
3 2 g Fe ₂ (SO ₄) ₃ 6 H ₂ O	33	21	18	17	18	5
2 3 g FeCl ₃ 6 H ₂ O	109	81	23	26	56	24
2.0 g AlCl ₃ 6 H ₂ 0	273	205	96	41	95	60
2.0 g ZnSO ₂ 7 H ₂ O	320	198	102	48	55	54
3 0 g MgS04 7 H20 5 4 g Al2(504)3 18 H20	337	166	48	27	62	23
5 4 g Al ₂ (\$0 ₄) ₃ ~18 H ₂ 0	106	95	16	33	118	74
5 7 g Al ₂ (50 ₄) ₃ (NH ₄) ₂ 50 ₄ 24 H ₂ 0	138 	77	60	21	60	65
3 5 g На ₂ НОР ₄	410	184	202	38	116	11

Batch Composition Soil H, 2% Annline-Furfural Resin (70 30) Approximately 1/40 mole of salt as shown.

TABLE 17

THE EFFECT OF FOAMING AGENTS ON THE QUALITY
OF 1 3 ANILINE-FURFURAL RESIN

		Compressive Strength in Lbs/Sq In									
Foaming Agent	Dry	Wet	Wet 1 W~D	₩et 4 ₩-D	Wet 1 F-T	Wet 4 F-T					
None A A(1) B C D E	163 43 55 55 61 89 80 39	35 10 21 6 9 14 13	55 38 24 12 20 17 11 23	59 14 10 11 13 50 17	25 10 16 6 8 11 7	12 6 12 ** 3 8 6					

** Failed (1) Heat treated 16 hours at 75 C

Batch Composition Soil F, 2% Aniline-Furfural Resin
(1 3) Foaming agent as shown

Composition of Foaming Agents

 $A = 4g \text{ NaHCO}_3 + 2g \text{ NH}_4\text{Cl}$

 ${\tt B}=3{\tt g}~{\tt CaC_2}~{\tt with}~{\tt Vinsol}$

 $C = 2 3g \text{ NaNO}_2$

 $D = 2 3g \text{ NaNO}_2 + 2g \text{ urea} + 1 8g \text{ NH}_4\text{Cl} + \text{Formalin}$

 $E = 2 3g \text{ NaNO}_2 + 2g \text{ urea} + 1.8g \text{ NH}_2\text{Cl} + \text{Furfural}$

 $F = 2 3g \text{ NaNO}_2 + 2g \text{ urea} + 1 8g \text{ NH}_4\text{Cl}$

TABLE 18

THE EFFECT OF FOAMING AGENTS ON THE QUALITY OF 70 30 ANILINE-FURFURAL RESIN

	Compressive Strength in Lbs/Sq In								
Foaming Agent	Dry	Wet	Wet 1 W-D	Wet 4 W-D	Wet 1 F-T	Wet 4 F-T			
None A A(1) B C D E	331 311 150 147 510 535 581	201 122 230 35 186 111 85	80 71 77 24 139 103 88	119 75 82 21 53 58 69	133 70 60 16 53 62 33	83 52 45 15 36 34 19			

(1) Heat treated 16 hours at 75°C

Batch Composition Soil H, 2% Aniline-Furfural Resin
(70 30) Foaming agent as shown

Composition of Foaming Agents

 $A = 4g \text{ NaHCO}_3 + 2g \text{ NH}_4 \text{ Cl}$

 $B = 3g \text{ CaC}_2$ with Vinsol

 $C = 2 3g \text{ NaNO}_2$

 $D = 2 3g \text{ NaNO}_2 + 2g \text{ urea} + 1 8 \text{ NH}_4\text{Cl} + 4g \text{ Formalin}$

 $E = 2 3g \text{ NaNO}_2 + 2g \text{ urea} + 1.8g \text{ NH}_2\text{Cl} + 3g \text{ Furfural}$

TABLE 19

THE EFFECTIVE ESS OF TWO PERCENT OF ANILINE-FLRFURAL RESIN (70 30) IN THE STABILIZATION OF SOIL B AS A FUNCTION OF THE ACIDITY OR ALKALINITY OF THE MEDIA

	Сол	press	ıve Str	ength 1	n Lbs/S	iq In
Catalyst	Dry	Wet	Wet 1 W- D	Wet 4 W-D	Wet 1 F-T	Wet 4 F-T
None	556	460	359	521	248	93
3 cc Conc HCl	540	403	441	425	243	89
1 5 cc Conc 4Cl	547	282	384	383	278	67
2 cc 10% NaOH Sol	592	434	315	316	200	80
6 cc 10% NaOH 5ol	600	362	140	496	7 9	41
10 cc 10% NaOH Sol	672	350	263	486	188	67

Batch Composition Soil B, 2% Aniline-Furfural Resin (70 30) Amounts of catalyst shown were added to 2500 g of soil

THE EFFECTIVENESS OF TWO PERCENT OF ANILINE-FURFURAL RESIN (70:30) IN THE STABILIZATION OF SOIL E AS A FUNCTION OF THE ACIDITY OR ALKALINITY OF THE MEDIA

	Compressive Strength in Lbs/Sq In.								
Catalyst	Dry	Wet	Wet 1 W-D	Wet 4 W-D	Wet 1 F-T	Wet 4 F-T			
None 3 cc Conc. HCl 1.5 cc Conc. HCl 2 cc 10% NaOH 6 cc 10% NaOH	702 280 208 561 803 743	528 220 313 441 418 406	203 77 184 181 172 219	518 162 328 213 770 626	282 173 204 261 133 223	137 86 146 161 85 77			

Batch Composition: Soil E, 2% Aniline-Furfural Resin (70:30). Amounts of catalyst shown were added to 2200 g of soil.

TABLE 21

THE EFFECTIVENESS OF TWO PERCENT OF ANILINE-FURFURAL RESIN (70:30) IN THE STABILIZATION OF SOIL G AS A FUNCTION OF THE ACIDITY OR ALKALINITY OF THE MEDIA

	Co	mpressi	ve Streng	th in L	bs/Sq_I	n.
Catalyst	Dry	Wet	Wet 1 W-D	Wet 4 W-D	Wet 1 F-T	Wet 4 F-T
None 3 cc Conc. HCl 1.5 cc Conc. HCl 2 cc 10% NaOH Sol. 6 cc 10% NaOH Sol.	884 834 1325 944 1395	-681 685 1044 445 657	642 704 1174 979 613	477 512 555 679 1087	395 402 563 401 451	132 206 259 209 170

Batch Composition: Soil G, 2% Aniline-Furfural Resin (70:30). Amounts of catalyst shown were added to 2520 g of soil.

TABLE 22

THE EFFECTIVENESS OF TWO PERCENT OF ANILINE-FURFURAL RESIN (70:30) IN THE STABILIZATION OF SOIL H AS A FUNCTION OF THE ACIDITY OR ALKALINITY OF THE MEDIA

	Compressive Strength in Lbs/Sq In.							
Catalyst	Dry	Wet	Wet 1 W-D	Wet 4 W-D	Wet 1 F-T	Wet 4 F-T		
None 3 cc Conc. HCl 1.5 cc Conc. HCl 2 cc lO% NaOH Sol. 6 cc lO% NaOH Sol. 10 cc lO% HaOH Sol.	396 132 207 210 272 452	211 79 128 106 20 62	96 65 67 44 75 77	54 20 11 39 63 45	91 32 76 32 14 23	83 19 46 17 6		

Batch Composition: Soil H, 2% Aniline-Furfural Resin (70:30). Amounts of catalyst shown were added to 2100 g of soil.

TABLE 23

THE EFFECTIVENESS OF TWO PERCENT OF ANILINE-FURFURAL RESIN (70:30) IN THE STABILIZATION OF SOIL L AS A FUNCTION OF THE ACIDITY OR ALKALINITY OF THE MEDIA

	Compressive Strength in Lbs/Sq In.							
Catalyst	Dry	Wet	Wet 1 W-D	Wet 4 W-D	Wet 1 F-T	Wet 4 F-T		
None 3 cc Conc. HCl 1.5 cc Conc. HCl 2 cc 10% NaOH Sol. 6 cc 10% NaOH Sol. 10 cc 10% NaOH Sol.	478 221 453 562 611 506	377 348 372 411 269 157	172 117 75 78 69 112	513 398 350 353 299 316	162 93 196 143 99 149	51 85 82 43 48 49		

Batch Composition: Soil L, 2% Aniline-Furfural Resin (70:30). Amounts of catalyst shown were added to 2200 g of soil.

TABLE 24

THE EFFECTIVENESS OF TWO PERCENT OF AMILINE-FURFURAL RESIN (70:30) IN THE STABILIZATION OF SOIL M AS A FUNCTION OF THE ACIDITY OR ALKALINITY OF THE WEDFA

	Compressive Strength in Lbs/Sq In.								
Catalyst	Dry	₩et	Wet 1 W-D	Wet 4 W-D	Wet 1 F-T	Wet 4 F-T			
None 3 cc Cenc. HCl 1.5 cc Conc. HCl 2 cc 10% NaOH Sol. 6 cc 10% NaOH Sol. 10 cc 10% NaOH Sol.	1124 907 820 956 827 815	249 589 139 405 184 214	109 189	1196 948 499 702 445 198	175 182, 17 83 82 135	35 78 5 22 15 26			

Batch Composition: Soil M, 2% Aniline-Furfural Resin (70:30). Amounts of catalyst shown were added to 2200 g of soil.

TABLE 25

THE EFFECTIVENESS OF TWO PERCENT OF ANILINE-FURFURAL RESIN (70:30) IN THE STABILIZATION OF SOIL N AS A FUNCTION OF THE ACIDITY OR ALKALINITY OF THE MEDIA

	Compressive Strength in Lbs/Sq In.								
Catalyst	Dry	Wet	Wet 1 W-D	Wet 4 W-D	Wet 1 F-T	Wet 4 F-T			
None 3 cc Conc. HCl 1.5 cc Conc. HCl 2 cc 10% NaOH Sol. 6 cc 10% NaOH Sol. 10 cc 10% NaOH Sol.	1273 947 1003 1060 1208 1019	981 797 771 643 638 443	1263 808 835 782 942 804	884 722 247 436 713 210	99 448 178 419 178 248	105 90 54 96 22 25			

Batch Composition: Soil N, 2% Aniline-Furfural Resin (70:30). Amounts of catalyst shown were added to 2200 g of soil.

TABLE 26

THE EFFECTIVENESS OF TWO PERCENT OF ANILINE-FURFURAL RESIN (70 30) IN THE STABILIZATION OF SOIL P AS A FUNCTION OF THE ACIDITY OR ALKALINITY OF THE MEDIA

	Compressive Strength in Lbs/Sq In							
Catalyst	Dry	Wet	Wet 1 W-D	Wet 4 W-D	Wet l F-T	Wet 4 F-T		
None 3 cc Conc HCl 1 5 cc Conc HCl 2 cc 10% NaOH Sol 6 cc 10% NaOH Sol 10 cc 10% NaOH Sol	494 414 412 496 503 561	173 283 318 298 31 181	252 158 356 298 99 45	284 188 256 198 198 167	135 149 165 140 83 92	59 99 130 78 17 45		

Batch Composition Soil P, 2% Aniline-Furfural Resin (70 30) Amounts of catalyst shown were added to 2360 g of soil

TABLE 27

THE EFFECTIVENESS OF TWO PERCENT OF ANILINE-FURFURAL RESIN (70 30) IN THE STABILIZATION OF SOIL U AS A FUNCTION OF THE ACIDITY OR ALKALINITY OF THE MEDIA

-	Compressive Strength in Lbs/Sq In							
Catalyst	Dry	Wet	Wet 1 W-D	Wet 4 W-D	Wet 1 F-T	Wet 4 F-T		
None 3 cc Conc, FCl 1 5 cc Conc HCl 2 cc 10% NaOH Sol 6 cc 10% NaOH Sol 10 cc 10% NaOH Sol	622 482 436 277 406 553	310 200 48 ** 68	536 370 309 38 134 191	466 222 314 29 201 137	185 96 121 10 45 13	43 25 28 5 ***		

**Falled

TABLE 28

THE EFFECTIVENESS OF TWO PERCENT OF AMILINE-FURFURAL RESIN (70 30) IN THE STABILIZATION OF SOIL V AS A FUNCTION OF THE ACIDITY OR ALKALINITY OF THE MEDIA

	Compressive Strength in Lbs/Sq In							
Catalyst	Dry	Wet	Wet 1 W-D	Wet 4 W-D	Wet l F-T	Wet 4 F-T		
None 3 cc Conc HCl 1 5 cc Conc HCl 2 cc 10% NaOH Sol 6 cc 10% NaOH Sol 10 cc 10% NaOH Sol	749 935 1147 1143 915 1089	468 530 512 276 500 528	664 386 242 51 222	223 ** ** ** 25 **	72 86 40 18 24 45	12 19 13 9 16		

**Failed

TABLE 29

THE EFFECTIVE ESS OF TWO PERCENT OF ANILINE-FURFURAL RESIN (70 30) IN THE STABILIZATION OF 10 SOILS - 4" x 6" SPECIMENS

					D1 up ro=	Load in	The	
Soll		After Di	fferent	Condition	_		LUS	
	la	1	2	3	4	5	6	7
H	360	767	358	669	329	852	175	442
Р	2041	1327	554	1102	493	1144	941	1136
В	2039	1588	584	1488	565	1515	987	1549
E	2446	1339	613	1313	638	1527	991	1591
I.	2812	2442	820	1911	360	942	1376	⊥648
G	2216	1991	727	2083	539	1681	1098	1987
บ	2364	1880	602	1784	429	1568	1240	1665
м	2065	1201	367	1025	397	685	298	860
N	1552	1286	350	1516	160	623	31	476
Δ	1701	1936	886	2348	351	2024	311	1164

Batch Composition 2% Aniline-Furtural Resin (70 30)

Conditions of Treatment

All specimens were air-dried for three days, dried to constant weight in an oven and then subjected to the different conditions of treatment described below

- la Untreated specimen No further exposure tested dry
- 1 No further exposure tested dry
- 2 10 days capillary absorption tested wet
- 3 10 days capillary absorption, and re-drying in oventested dry
- 4 10 days capillary absorption and 12 cycles of freezing and thawing tested wet
- 5 10 days capillary absorption, 12 cycles of freezing and thawing, and re-drying in oven-tested dry
- 6 10 days capillary absorption, and 12 cycles of wetting and drying tested wet
- 7 10 days capillary absorption, 12 cycles of wetting and drying, and re-drying in oven-tested dry

TABLE 30

COMPARISON OF THE SOIL STABILIZING EFFECTIVENESS
OF ANILINE-FURFURAL (70 30), RESIN STABILIZER 321, AND
PORTLAND CEMENT

		Compressive Strength in Lbs/Sq In					
5 011	Type of Admixture	Dry	Wet	1 Wet 1 W-D	₩et 4₩-D	Wet 1 F-T	Wet 4 F-T
н	Anılıne-Furfural	396	211	96	54	91	83
	Resın 321	17	3	44	**	**	**
	Portland Cement	106	61	59	54	47	37
P	Anılıne-Furfural	494	173	252	284	135	59
	Resın 321	95	41	91	29	8	1
	Portland Cement	185	98	73	97	80	92
В	Annline-Furfural	556	460	359	521	248	93
	Resin 321	255	157	163	156	53	7
	Portland Cement	420	269	178	397	225	198
E	Aniline-Furfural	702	528	203	518	282	137
	Resin 321	341	187	210	141	89	34
	Portland Cement	307	171	146	141	119	83
L	Amline-Furfural	478	377	172	513	162	51
	Resin 321	413	142	178 (1	.) 258	48	7
	Portland Cement	350	227	153	185	154	148
G ~	Anılıne Furfural	884	681	642	477	395	132
	Resın 321	390	57	121	195	39	2
	Portland Cement	291	131	47	75	85	75
Ū	Anılıne-Furfural	622	310	536	466	185	43
	Resin 321	264	67	176	134	3	1
	Portland Cement	317	153	10 2	120	115	90
M	Aniline-Furfural	1124	249	515	1196	175	35
	Resin 321	425	234	233	308	73	4
	Portland Cement	367	181	112	97	103	111
N	Anılıne-Furfural	1273	981	1263	884	99	105
	Resin 321	645	195	306	20	86	2
	Portland Cement	470	206	95	118	142	96
7	Apılıne-Furfural	749	468	664	223	72	12
	Resin 321	384	110	142 (1	.) 67	20	1
	Portland Cement	370	177	127	130	128	117

(1) One test only **Failed

Batch composition Specimens treated with 2% Aniline-Furfural
Resin (70 30), 1% Resin 321, and 6% Portland Cement respectively

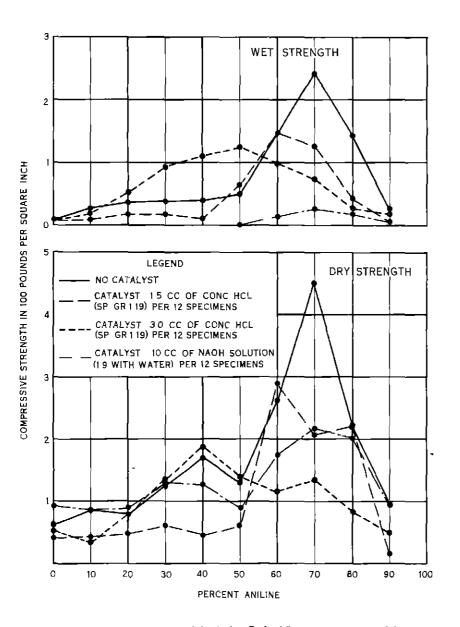


Figure 2 The Effect of the Aniline Furfural Ratio on the Quality of the Resinous Cement in Acid, Basic and Neutral Media

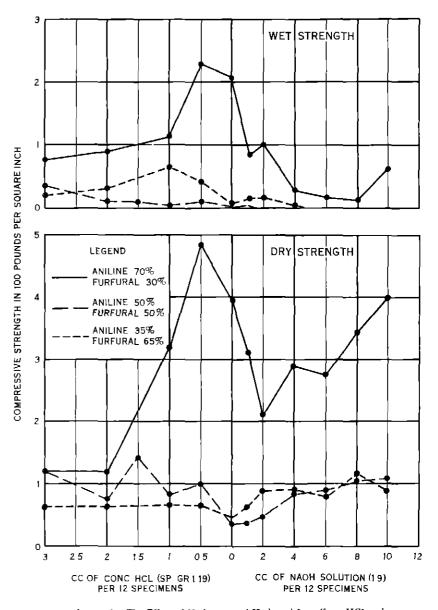


Figure 3 The Effect of Hydrogen and Hydroxyl Ions (from IIC1 and NaO1I) on Three Aniline Furfural Resins

TABLE 33

STRUCTURE STUDIES ON ANILINE-FURFURAL RESINS THROUGH THE USE OF DIMETHYLANILINE AND P-TOLUIDINE IN REACTION WITH FURFURAL

		Com	pressiv	e Strengt	th in Lb	s/5g In	
Resin Material	Catalyst	Dry	Wet	Wet 1 W-D	Wet 4 W-D	Wet 1 F-T	Wet 4 F-T
2 l Anılıne-Furfural	None	393	276	101	21	124	82
2 l Anılıne-Furfural	3 cc HCl Conc	132	64	34	l 17	43	31
2 l Anılıne-Furfural	10 cc 10% NaOH	103	8	19		8	ગ્નૃત
2 1 Dimethylaniline-Furfural	None	31		٦,	-≍	_1/ ₂	} ~⊁
2 l Dimethylaniline-Furfural	3 cc HCl Conc	18	₩ ×	⊰ત	-4	بہ	-;⁄
2 l Dimethylariline-Furfural	10 cc 10% NaOH	60		4	7 . 7	≯ '_}	≴∽ւ
70 30 p-Toluidine-Furfural	None	19	5	31	16	7	4
35 65 p-Toluidine-Furfural	None	18	6	38	16	2	4⊬ ×
50 50 p-Toluidine-Furfural	None	94	47	37	31	33	28
70 30 p-Toluidine-Furfural	3 cc HCl Conc	108	74	31	29	52	40

∺¥Faıled

Batch Composition Soil H, 2% Resinous Material Arounts of catalyst shown were added to 2100 g of soil

TABLE 34

TIE EFFECTIVENESS OF LREA-FLRFLRAL RESINS

		Com	pressiv	e Strengt	th in Lb	s/Sq In	
Resin Material	Catalyst	Dry	Wet	Dry 1 W-D	Dry 4 W-D	Wet l F-T	Wet 4 F-T
l l Urea-Furfural	3 cc HCl Conc	46	6	80	30	22	2
1 2 Urea-Furfural) 1 3 Anılıne-Furfural)	3 cc HCl Conc	118	73	100	44	26	24

Batch Composition Soil H, 2% Pesinous Material Amounts of catalyst shown were added to 2100 g of soil

TABLE 35

THE EFFECTIVENESS OF DIFFERENT AMOUNTS OF FURFURAL ADDED TO URINE AND BELRO ROSIN IN THE STABILIZATION OF SOIL G

Urine cc	Furfural g	Dry	Wet	Compre Wet 1 W-D	ssive Str Wet 4 W-D	ength in Wet 1 F-T	Lbs/Sq In Wet 4 F-T
260 260 260 260 130 130 130 130	12 8 9 6 6 4 3 2 6 4 4 8 3 2 1 6	878 972 936 1026 1028 1156 1220 925	659 715 389 615 17 545 631 175	599 558 518 70 7 558 259	407 415 305 ** 494 497 118	154 266 159 189 3 148 212 33	15 33 17 20 ** 15 20

~~Failed

Batch Composition 2520 g Soil G, 50 g Belro Rosin Amount of urine and furfural per batch as shown

TABLE 36

THE EFFECTIVENESS OF PHENOL-FURFURAL RESINS

		Comp	pressiv	e Strengt	th in Lb	s/Sq In	
Resin Material Molar Ratio	Catalyst	Dry	Wet	Wet 1 W-D	Wet 4 W-D	Wet 1 F-T	Wet 4 F-T
1 2 Phenol-Furfural	5 cc HCl Conc	12	**	**	*~	ત્ય	**
1 1 Phenol-Furfural	20 cc 10% NaOH	53	**	*-	4-34	×̈ν	**
l 2 Anılıne-Furfural) l 2 Phenol-Furfural)	4 cc HCl Conc	52	24	33	36	20	11
1 2 Aniline-Furfural) 1 2 Phenol-Furfural)	4 cc HCl Conc	79	32	59	49	22	15

ند Failed

Batch Composition Soil H, 2% Resinous Material. Amounts of catalyst shown were added to 2100 g of soil

TABLE 37
THE EFFECTIVENESS OF UREA-FORMALDEPYDE RESINS

		0	ompress	sive Str	ength in	Lbs/Sq	ln .
Percent Resin	Catalysts Added	Dry	Wet	Wet 1 W-D	Wet 4 W-D	Wet 1 F-T	Wet 4 F-T
2	05g NH,Cl	239	9	90	74	56	16
2 (1)	05gNH/Cl	140	12	44	31	14	8
2 (1) 2	2 O g Resorcinol O 5 g NH4Cl	255	16	127	84	15	10
1	3 5 g Resorcincl O 25 g NF Cl	199	15	93	116	14	12
1	l 7 g Resorcinol O 25 g NF _A Cl	96	7	64	35	2	<u> </u>
1	0 25 g NH/Cl	65	*	₽ ⊁	**	***	يانو
1 5	2 5 g Resorcinol O 4 g NH _A Cl	115	11	92	77	11	7
1 5 2	04g NH/Cl	122	15	81	54	6	2
2	0 5 g NH <u>/</u> Cl 2% Armour Amine 1180 B Lot 601 7	19 	10	13	9	11	10
2	0 5 g NH4Cl 2% Armour Amine Coco B Lot 390 l	26	5	11	11	8	12
2	1 0 g NH4Cl 3 5 g Resorcinol 1 g NaHCO3	69	16	97	60	14	7

** Failed

Batch Composition Soil H, percent Resin Solution (1 part of urea to 2 parts of formalin) Amounts of catalyst shown were added to 2100 g of soil

⁽¹⁾ The resin was reacted in the usual way (1 part urea to 2 parts formalin reacted at 50-55°C) Fowever, the resin was then cried and added in the powdered form instead of the usual reaction solution

TABLE 38

THE EFFECTIVENESS OF SMALL PERCENTAGES OF UREA-FORMALDEHYDE RESIN IN THE STABILIZATION OF SELECTED SOILS

				Compressi	ve Strengt	h in Lbs/Sq In
Soil	Dry	Wet	Wet 1 W-D	Wet 4 W-D	Wet 1 F-T	Wet 4 F-T
E H N P	474 60 1039 390 735	151 5 *+ 9	66 17 ** 7	40 6 ** 5	28 4 ** 3 **	25 2 ** 3 **

-* Failed

Batch composition 20g Urea + 60cc 37% Formalin (makes 1 2 to 1 3% Dimethylolurea Resin for each batch)
Soil as shown

TABLE 39

THE EFFECTIVENESS OF WELDWOOD GLUE IN THE STABILIZATION OF SELECTED SOILS

_				Compress	sive Stren	gth in Lbs/Sq In
Soll	Dry	Wet	Wet 1 W-D	Wet 4 W−D	Wet 1 F-T	Wet 4 F-T
E	169	**	%	**	- 11×	3-¥
H	62	8	16	3	4	3
N	567	₩₩	₃⇒	∺	**	**
P	133	C) E	7×	-ىږ	- ←≻	**
V	659	**	***	~ي	, ←×	**

** Failed

Batch composition 40g of Weldwood glue per batch (approximately 1 8%) Soil as shown

TABLE 40

THE EFFECTIVENESS OF CALCIUM SULFAMATE—FORMALDEHYDE RESIMANT (1) IN THE STABILIZATION OF SOILS MAND E

		Compre	ssive Stre	ngth in Lb:	s/Sq In	
Resin Added to Neutralize	Dry	Wet	Wet 1 W-D	Wet 4 W-D	Wet 1 F-T	Wet 4 F-T
	9	Soil E				
Total base exchange ions Total Ca ions Protal base exchange ions Ca ions	215 193 264 262	10 8 4 3	86 34 7	2 1 ***	5 3 3 1	3 3 3 2
	S	Soil M				
Total base exchange ions 1/2 Total base exchange ions 1/2 Ca ions	196 310 344	38 3 -	3	1 *- ኦዓ	3 *	2 2 3

⁽¹⁾ Sulfamic acid and formaldehyde were added on the basis of the base exchange ions which might be supplied to the resin **Failed

TABLE 41

THE EFFECTIVENESS OF ANILINE-FURFURAL RESIN IN CONJUNCTION WITH VINSOL AND CONGO RESINS

Soll	Natural Resin Added	Aniline-Furiural Added (1)	Dry	Wet	Compress:	ve Streng Wet	th in Lbs	/Sg In
		%			1 W-D	4 W-D	1 F-T	4 F-T
H	1% Congo TV2 1% Congo No. 28 1% Congo PC1 1% Vinsol None	1 1 1 2	58 82 126 77 283	10 11 63 39 265	6 7 48 12 116	9 14 31 13 67	2 7 29 6 60	, 56 2 92
E	1% Congo TV2 1% Congo PC1 1% Congo No 28 1% Vinsol None	1 1 1 2	804 741 720 820 970	618 699 536 561 789	425 650 248 380 702	505 691 510 407 434	191 298 249 231 413	132 136 59 51 256
M	1% Congo TV2 1% Congo No 28 1% Congo PC1 1% Vinsol None	1 1 1 1 2	909 902 1095 1061 911	679 623 819 833 779	703 734 800 979 802	621 568 785 796 650	229 238 321 303 330	32 27 10 62 106
L	1% Congo TV2 1% Congo No 28 1% Congo PC1 1% Vinsol None	1 1 1 1 2	934 766 874 783 788	660 134 570 489 578	938 52 283 31 675	288 296 692 398 666	223 16 230 165 283	57 7 90 53 182

∺Failed

(1) V ratio of aniline-furfural Percentage added is based on the dry weight of soil used

TABLE 42
ANTLINE_FURFURAL RESIN CATALYZATION

l	Result					
Salt	No Water	2 cc Water				
None (Control) FeCl ₃	Soft, viscous liquid Good hardening over night	Soft, viscous liquid Harder than control but still soft				
AlCl ₃	Good hardening over night	Became thick after 30 minutes Good brittle resir				
BaCl ₂	No effect - same as centrol	No eifect - same as control				
FeSO ₄	Very little effect al- most same as control	Very little effect, same as control				
NaCl	No effect - same as control	No effect - same as control				
РьО	54.0 (C1	No effect - same as control				
н ₃ РО ₄	Immediate precipitate of amiline phosphate					
H ₃ PO ₄ + AlCl ₃	Transpired proopries	Immodiate precipitate of aniline phosphate Rest of mixture re- maired soft				

TABLE 43
ANILINE-FURFURAL RESIN CATALYZATION

Catalytic Solution-cc	Effect
1/4 1/2 1 2 3 4	AlCl3 Very slow hardening Brittle resin after one day Faster hardening Good resin formed in 18 hours Good resin formed over night Brittle solid in less than two hours Resin formed immediately Resin formed immediately
1/4 1/2 1 2 3 4 5	FeCl3 Slow hardering into brittle resin Good resin formed over night Good resin formed overright Harder resin than given with 1/2 co of FeCl3 Good resin in several hours Rapid resin formation Very ratio colidification Very ratio solidification

 $\begin{array}{c} \underline{\text{Catalytic Solutions}} \\ \underline{\text{log FeCl}_3} & 6 \text{ H}_2\text{O} + 20 \text{ cc H}_2\text{O} \\ \underline{\text{log AlCl}_3} & 6 \text{ H}_2\text{O} + 25 \text{ cc H}_2\text{O} \end{array}$

Batch Composition
13 7 cc Aniline
6 7 cc Furfural

 $\underline{\rm Mote}$. Aluminum salt generally did better than iron salt. The more salt in either case, the quicker and more brittle the rosin formed

TABLE 44
ANILI (E-FURFURAL PESIU CATAL ZATIO)

Water cc	Effect				
No Emulsi ication	1/4 cc FeCl ₃ Solution	1/4 cc AlCl ₃ Solution			
one (Control)	Resin formed but re- mained fairly soft	Brittle resin formed slowly one day			
5	Pasan formed but was slightly softer than control	Resin 'ormed but re- mained fairly soit in- stead of hardening as in the control			
10 15	Recam format under a	Resum formed under a			
20 25	layer of water be- coming increasingly softer the wore water used	layer of water be- coming ircreasingly softer the more water used			

Cstalytic Solutions
10g FeCl3 6 H2C + 20 cc H2C
10g AlCl3 6 F2C + 25 cc H2C

Batch Composition
13 7 cc Aniline
6 7 cc Furfural

TABLE 45
ANILINE-FURFURAL RESIN CATALYZATION

Catalyst	H ₂ O Content	Effect
1/4 cc AlCl ₃ Sol added before emul- sification	400 cc	Remained emulsified and formed slight precipitation on bottom
1/4 cc FeCl ₃ Sol added before emul- sification	400 cc	Emulsion broke and a floccu- lent precipitate was formed which floated on the top of
1/4 cc AlCl3 Sol added to portion of sample after emulsi- fication	400 cc	the aqueous solution Sample came through in a white milky emulsion which turned pink upon addition of AlCl3 with formation of floce-
1/4 cc FeCl ₃ Sol acded to portion of sample after emulsi- fication	400 cc	ulent precipitate Sample was milky when emulsi- fied (as above) but turned brown upon addition of FeCl3 with formation of brown flocculent precipitate

 $\begin{array}{c} {\rm Catalytic~Solutions} \\ {\rm l0g~FeCl}_3 ~ 6 ~ {\rm F}_2{\rm O} + 2{\rm O} ~ {\rm cc} ~ {\rm H}_2{\rm O} \\ {\rm l0g~AlCl}_3 ~ 6 ~ {\rm H}_2{\rm O} + 2{\rm 5} ~ {\rm cc} ~ {\rm h}_2{\rm O} \end{array}$

Batch Composition
13 7 cc Aniline
6 7 cc Furfural
Varied water content (Emulsified)

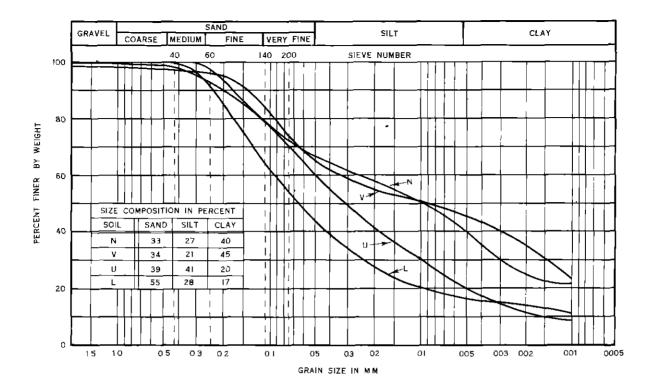
Note 1. The addition of larger amounts of catalyst in duplicate of the last two tests yielded a faster reaction with a brighter color Note 2 It was found that the addition of a small amount of soap prevented the emulsion from reacting while in the emulsifier

TABLE 46
ANILINE-FURFURAL RESIN CATALYZATION

Water Content-cc	Effect	
	Catalyst 1/4 cc of FeCl3 Solution	
None	Soft resin formed in one hour (catalyst may not	
(Control)	have been thoroughly mixed)	
5	Viscous liquid, later developed into a soft	
	resin water collecting at the center	
1.0	Liquid, thicker scum on top later became gummy	
3.5	with small spots of floccules	
15	Emulsion broken after about 2 hours, flocculent precipitate	
20	Emulsion broken after about 2 hours, flocculent	
	precipitate	
25	Emulsion broken after about 1 hour, flocculent	
	precipitate	
	Cotalyst 1// as of AlCl Solution	
None	Catalyst 1/4 cc of AlCl ₃ Solution Immediate formation of a fairly hard brittle	
(Control)	resin	
5	Very viscous resin from which water could be	
	squeezed, showing emulsion had not been broken	
10	All had broken from emulsion in 2 hours These	
J .	samples showed much less tendency to be floccu-	
	lated than those treated with FeCl3 A resin of	
	somewhat gummy texture was formed at the bottom	
	of the cup becoming increasingly softer and lighter in color with samples having increasing	
}	water contents.	

Catalytic Solution 10g FeCl₃ 6 H₂0 + 20 cc H₂0 10g AlCl₃ 6 H₂0 + 25 cc H₂0

Batch Composition
13 7 cc Aniline + 6.7 cc Furfural
Varied water content (emulsified)



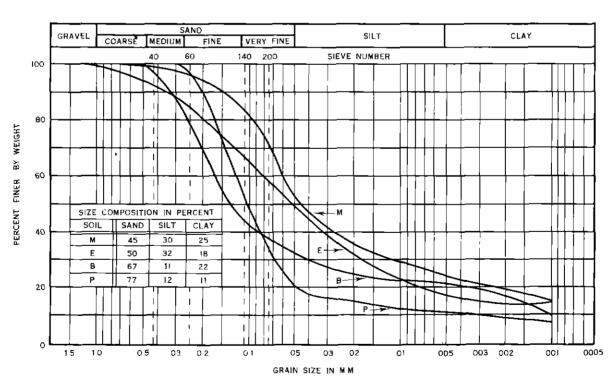


Figure 1 Grain Size Distribution of the Different soils

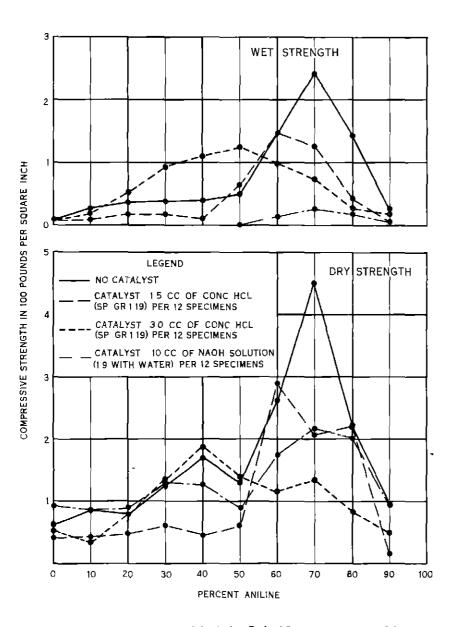


Figure 2 The Effect of the Aniline Furfural Ratio on the Quality of the Resinous Cement in Acid, Basic and Neutral Media

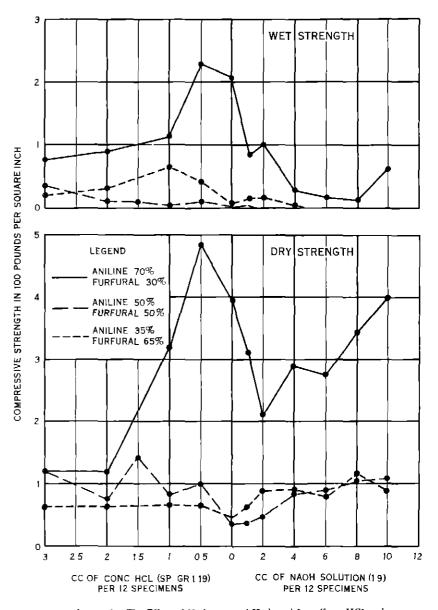


Figure 3 The Effect of Hydrogen and Hydroxyl Ions (from IIC1 and NaO1I) on Three Aniline Furfural Resins

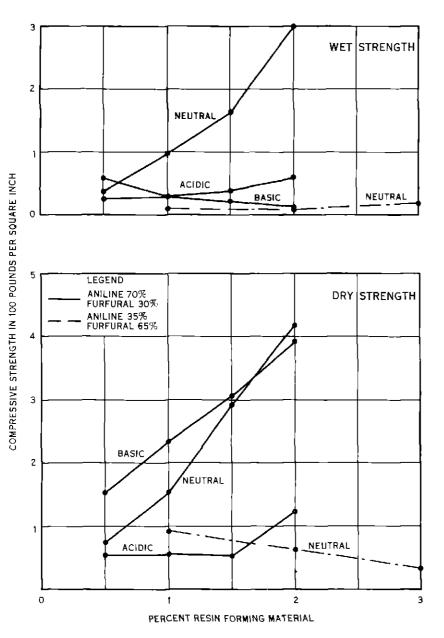


Figure 4 The Effectiveness of Low Percentages of Aniline Furfural Resins

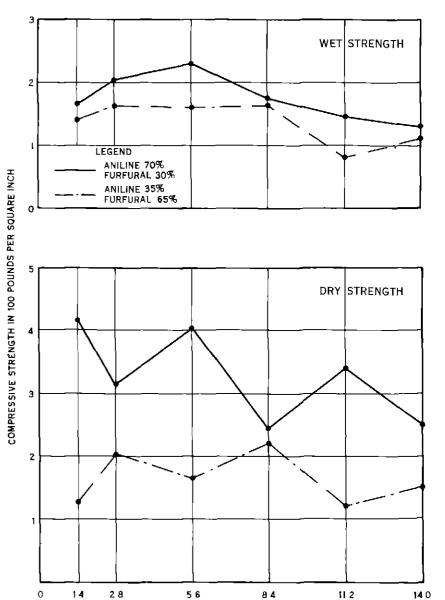
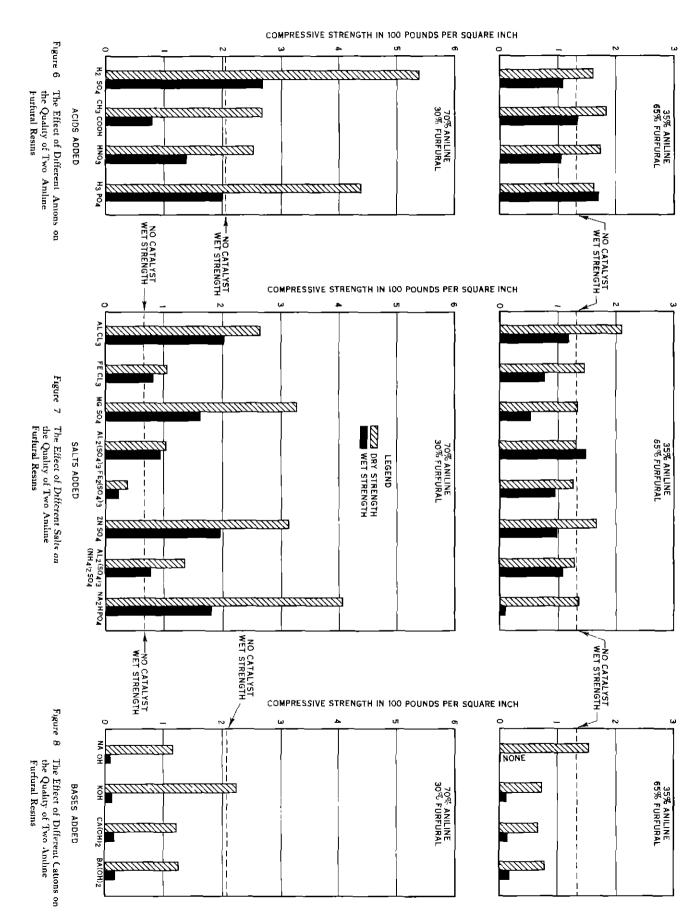


Figure 5 The Effect of Different Amounts of Sulfuric Acid on Two Aniline Furfural Resins

WEIGHT OF H2504 IN GRAMS



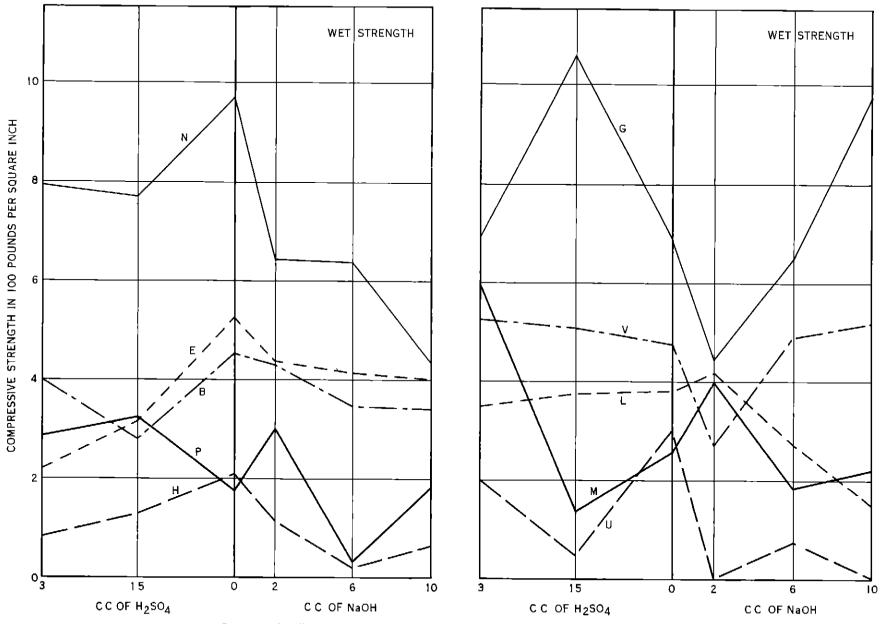


Figure 9 The Effectiveness of Two Percent Aniline Lurfural Resin(70 30) in the Stabilization of Ten Soils as a Function of the Acidity or Alkalinity of the Media 2" x 2" Specimens

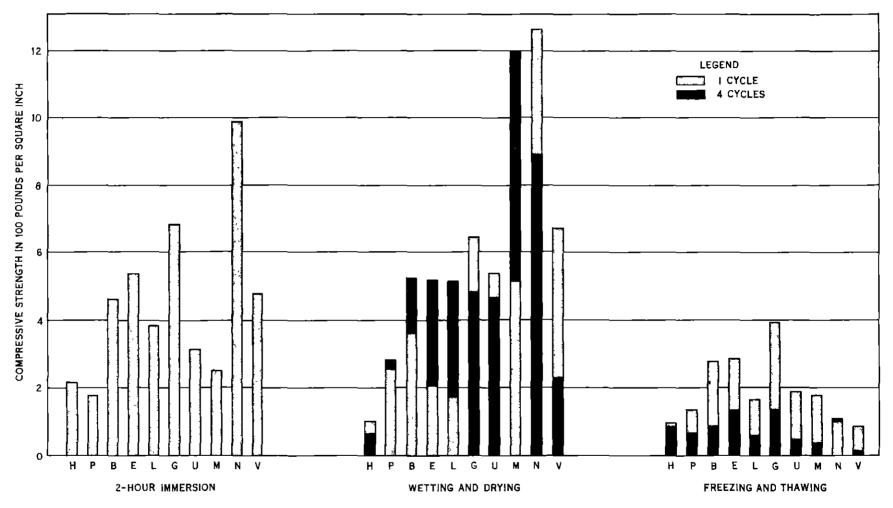


Figure 10 The Effectiveness of Two Percent Aniline Furfural Resin (2 1) in the Stabilization of Ten Soils (No Catalyst) 2" x 2" Specimens



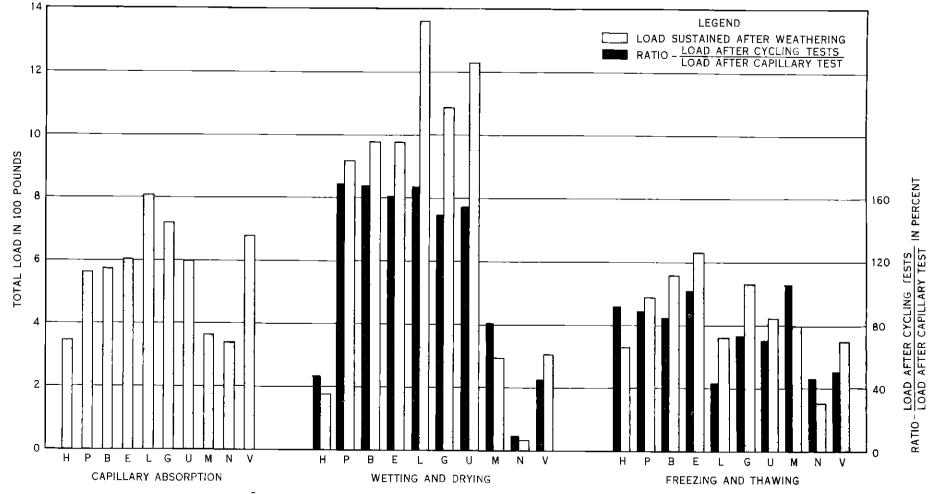


Figure 11 The Effectiveness of Two Percent Aniline Furfural Resin (2.1) in the Stabilization of Ten Soils (No Catalyst) 4" x 6" Specimens