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A. R. Van Steenbergen

Department:

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THE EFFECT OF EPOXY RESINS ON THE PLASTICITY INDEX OF AN A-6 SOIL

BY

A. R. VAN STEENBERGEN, 1935

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THESIS

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Approved by

Thomas S. Fry (advisor)

Paul R. Munger

ABSTRACT

This thesis reports the results of an investigation of the variation in plasticity of a clayey soil after treatment with small quantities of epoxy resin and curing agent or with curing agent alone.

The series of samples tested consisted of an A-6 soil obtained from the vicinity of Rolla, Missouri, combined with:

1. 0-3% of triethylenetetramine hereafter referred to as TETA.
2. 0-3% of diethylenetriamine hereafter referred to as DETA.
3. 0-3% of Araldite 6010 resin cured with TETA. The TETA content was varied from 20% to 100% of the resin by weight.
4. 0-3% Araldite 6010 resin cured with DETA. The DETA content was varied from 20% to 100% of the resin by weight.

The plasticity index of the treated soil samples was computed by conventional soil testing procedures. The relative amount of unreacted amine remaining in samples was determined by titration.

Qualitative relationships were found between the plasticity index and the type and quantity of additive used. The complexities of these relationships are discussed and suggestions for further research are made.

ACKNOWLEDGMENT

The author wishes to thank his advisors, Dr. Thomas S. Fry of the Civil Engineering Department and Dr. Kenneth G. Mahan of the Chemical Engineering Department, for their wisdom and encouragement throughout this research. Also, Professor John B. Heagler, Jr. of the Civil Engineering Department whose frequent consultations and discussions were most helpful.

The author extends a special note of appreciation to his wife and children who created the stimulus and atmosphere without which this paper could not have been written.

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I. INTRODUCTION

Soil stabilization is the science of changing the physical properties of a soil to suit the needs of the engineer. It is not a new concept however. In 350 B.C., the Romans used sand-gravel-lime base courses in the construction of the Appian Way. In 150 B.C., they discovered a cheap substitute (in the form of a volcanic ash) for a portion of the lime. Stronger mortars were attainable with this ash because an insoluble precipitate was formed in the mix.

Since these early applications of soil stabilization techniques, man has strived constantly to find new and more effective additives for soil stabilization. The problem has been reduced to the point where the methods of soil stabilization can be segregated into four distinct categories (1).

1. Surface energy reduction, whereby the zeta potential of the clay is reduced to the point where a flocculant structure of the clay particles is attained.
2. A reaction between a single chemical additive and the soil constituents which generally refers to the reaction between an amorphous silicate and an alkali to produce an insoluble precipitate.
3. Chemicals that react with other added chemicals to form insoluble precipitates. An example of such a reaction is sodium silicate and calcium chloride which yields calcium silicate (the insoluble precipitate) and sodium chloride.
4. Chemicals that react with themselves in the presence of water or air to form insoluble precipitates such as hydrated lime or portland cement.

The purpose of this investigation is to evaluate qualitatively the effects of epoxy resins as a stabilizing agent for fine grained soils.

Epoxy resins are thermosetting materials that are cured by introducing a catalyst or curing agent to the resin. The resin is synthesized from epichlorohydrin or bisphenol A. The curing agent can be an amine, an amide, an organic acid, or an acid anhydride (2). Two primary aliphatic amines, TETA and DETA were used as curing agents for this investigation.

Cured epoxy resins exhibit many desirable properties. They are versatile in the sense that they can be engineered to meet a wide variety of specifications. The resins and curing agents have long shelf lives if properly synthesized. The cured system is tough, has low shrinkage, and is virtually invulnerable to caustic or acid attack (2).

In Civil Engineering, epoxy resins are used primarily as adhesives. They are used in the fabrication of laminates, repair of cracked concrete, bonding of new concrete to old and as additives in asphaltic and portland cement concrete. Very little research has been done in the past with epoxy resins as a stabilizing agent for soils, although, their effect in sand and, as this paper will demonstrate, in clay, is quite remarkable.

II. MATERIALS AND PROCEDURE

The soil used for this investigation is common to the area of Rolla, Missouri. Its physical properties are such that it would require stabilization if used in certain construction situations.

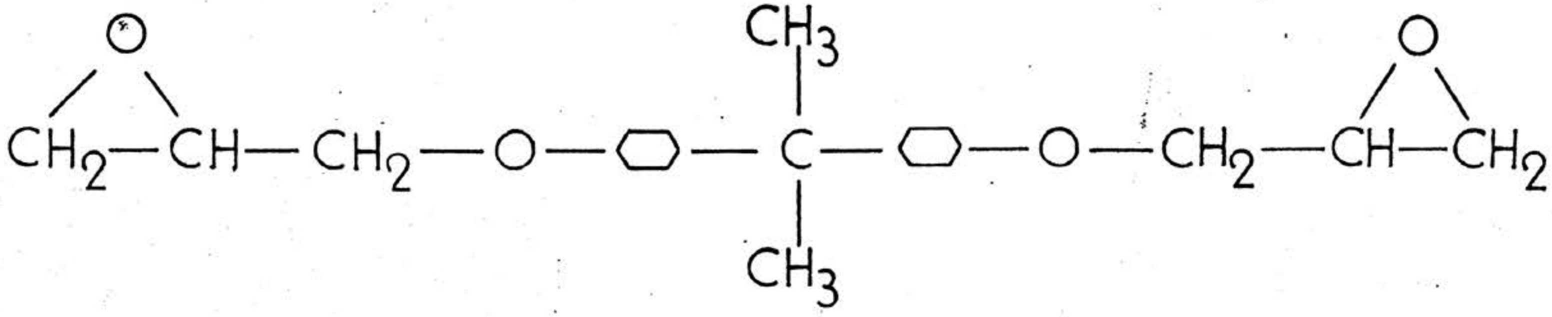
A grain size analysis and Atterberg Limit determination classified the soil as CL under the Unified Classification System. A liquid limit of 39, and a plastic limit of 20 results in a plasticity index of 19. This group of soil includes inorganic clays of low to medium plasticity, gravelly clays, sandy clays, silty clays and lean clays (3). The American Association of State Highway Officials (AASHO) Classification of this soil was A-6.

An X-ray diffraction analysis of this soil indicated that the predominant clay minerals were illite and chlorite.

Araldite 6010 was the only epoxy resin used. It is a common, general purpose resin manufactured by the CIBA Co., Inc. It has an epoxide equivalent of 195 and a viscosity of 16,000 centipoises at 25°C. (2).

The epoxide equivalent is the weight of resin in grams which contains one gram chemical equivalent of epoxy (2). A typical epoxy resin molecule in a simple and idealized form is represented by the diglycidyl ether of bisphenol A (See Figure 1).

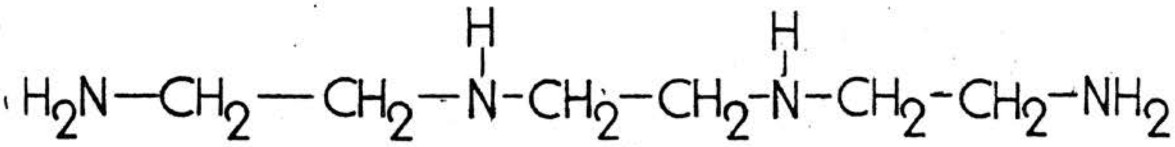
Two different primary aliphatic amines, TETA and DETA, were used to cure the resin. TETA has six available hydrogen ions and DETA has five (See Figure 2). Tertiary amines, acids, and anhydrides were not considered as curing agents for this project because their ate of reaction with epoxy resins at room temperature would be expected to be very slight and in some cases negligible.



THE DYGLYCIDYL ETHER OF BISPHENOL A

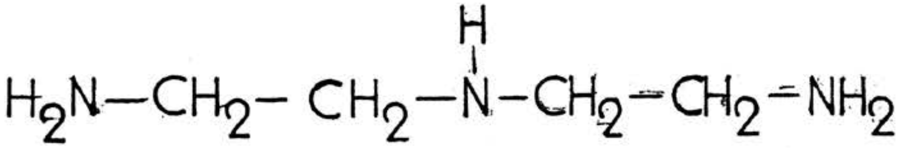
FIGURE 1. EPOXY RESIN MOLECULE

PRIMARY ALIPHATIC AMINES



$$H_2N-CH_2-CH_2-\overset{H}{\overset{|}{N}}-CH_2-CH_2-\overset{H}{\overset{|}{N}}-CH_2-CH_2-NH_2$$

TRIETHYLENETETRAMINE



$$H_2N-CH_2-CH_2-\overset{H}{\overset{|}{N}}-CH_2=CH_2=NH_2$$

DIETHYLENETRIAMINE

FIGURE 2. CURING AGENTS

Resins can be cured into thermoset compounds by three different reactions: (2)

1. Direct linkage between epoxy groups.
2. Linkage of epoxy groups with aromatic or aliphatic hydroxyls.
3. Cross linkage with the curing agent through various radicals.

Primary and secondary aliphatic amines including TETA and DETA fall into the crosslinking category of curing reactions.

Epoxy resins are cured by adding a specified amount of curing agent to the resin, mixing them thoroughly, and allowing the necessary time to elapse for the crosslinking reaction to take place. The theoretical amount of curing agent required is the stoichiometric amount and its determination is shown in the following example.

DETA has a molecular weight of 103. Since there are five hydrogen atoms attached to the three nitrogen atoms (See Figure 2), the equivalent weight per active hydrogen is 103/5 or 20.6. Since each active hydrogen can open one epoxy ring, 20.6 grams of DETA should be combined with one epoxide equivalent weight of resin. Araldite 6010 has an epoxide equivalent of 195. The theoretical or stoichiometric amount of DETA to be used per one hundred parts of resin is then 195/20.6 or approximately 10. This value must be checked in practice to insure adequate curing for the intended use of the cured compound (4).

The treated soils used in this study can be divided into two categories; that treated with the amine (curing agent), and that treated with both resin and amine.

Where used alone, the amine was first mixed with enough distilled water to produce a 20 percent moisture content in the soil sample. The amine-distilled water solution was then added to the dry soil.

When the resin and amine were both used as the additive, they were introduced into the soil in a slurry which consisted of amine, resin, distilled water and a small amount of the soil. The amount of distilled water used was sufficient to produce a moisture content of 20 percent in the sample. The use of a slurry facilitated the extraction of the sticky amine-resin mixture from the mixing apparatus. It also provided an adequate means of transporting the additive throughout the soil sample.

The amount of amine, when used alone, varied from 0-3 percent by the dry weight of the soil. The amount of amine-resin used also varied from 0-3 percent by the dry weight of the soil and the ratio of amine to the resin was varied also. These ratios were 25, 50, 75 and 100 parts of amine to 100 parts of resin.

Atterberg Limit determinations were performed on untreated soil, amine treated soil, and amine-resin treated soil. The samples containing amine alone were tested immediately after mixing whereas the amine-resin samples were allowed to cure for a period of seven days at room temperature.

The effect of the additives was measured by the computation of the plasticity index of each sample. After measuring the index properties, the soil samples were subjected to qualitative chemical tests in an effort to determine the relative amount of unreacted amine that remained in each sample.

The dry, treated soil samples were powdered using a mortar and pestle. Ten gram samples were weighed into clean beakers and 100 milliliters of distilled water (pH 5.9 ± 0.1) was added. The soil water mixture was stirred manually for ten minutes, the solids allowed to settle, and the pH of the decanted liquid determined.

Samples of the decanted liquid were titrated with a .497N hydrochloric acid using phenol red as an indicator. It was assumed that the unreacted or uncombined amine was converted to amine hydrochloride and the titrated hydrochloric acid was totally consumed in the reaction (5).

The amount of .497N hydrochloric acid required to titrate the unreacted amine was recorded and the data were used to determine the quantity of amine required to satisy the reactions taking place in the soil.

Results of the Atterberg limit tests are shown in Tables I through IV and the plasticity index are plotted on Figures 3, 5, 6, 7, and 8. Titration data are shown on Tables I through IV.

III. DISCUSSION AND RESULTS

A plasticity index reduction of the soil occurred when amine only was used as the stabilizing agent. This was expected because the amine contained reactive hydrogen which, according to Hofmeister's lyotropic series (6), is the most preferred cation for a negative sol such as a clay mineral-water mixture.

The pH of the untreated soil sample varied from 4.9 to 5.1 as compared to a pH of 5.9 for the distilled water used. One milliliter of either curing agent dissolved in one hundred milliliters of distilled water produced a solution which had a pH greater than 13. Therefore, small amounts of unreacted or uncombined amine were expected to give measurable pH differences. pH readings alone are not a true measure of the effectiveness of the ions present. Therefore, the titration data are a necessary supplement to the pH measurements (5).

The performance of the plastic limit tests on treated soil samples was very difficult. Soils of medium plasticity (if the moisture content is above the plastic limit) can be rolled out in threads smaller than 1/8 inch in diameter. The sample may then be remolded and rolled into a thread with a slightly greater diameter. With the treated soil samples in this investigation, plastic limit samples had to be rolled out with a moisture content well in excess of the plastic limit. Rolling had to be done slowly enough so that the moisture loss and proper thread diameter occurred at approximately the same time. If the 1/8 inch diameter required was passed, the sample could not be remolded and rerolled because of the excess moisture loss. This difficulty in the plastic limit determination contributed to the scatter of points on all curves.

The plasticity index is computed by subtracting the plastic limit from the liquid limit. A change in the plasticity index such as the reduction due to the addition of amine or amine-resin combinations could be caused by changes in the liquid limit, the plastic limit or both. The liquid limit throughout this series of tests remained fairly constant although there was a slight decrease at higher additive contents (See Tables I-IV and Figure 4).

The liquid limit determination in spite of the unique testing procedure, is a measure of shear strength at a certain moisture content. According to Lambe (7), an increase in shear strength can be caused by the substitution of a more preferential cation such as hydrogen. A decrease in shear strength can be caused by an increase in the pH of the pore fluid. Tables I-IV indicate the increase of pH.

According to A. Casagrande (8), the shear strength of the soil at the liquid limit is equal to approximately 1 gram per square centimeter. The data show (See Figure 4) that the liquid limit, between 0 and 1 percent amine content, remains relatively constant. It is evident, therefore, that the shear strength reduction due to the increase in the pH of the pore water and increase in shear strength due to cation exchange are offsetting reactions.

The increase in the plastic limit between 0 and 1 percent amine content is due to the fact that the surface charges on the clay particles are being satisfied by the addition of the amine, thereby reducing the cohesion. The soil mass then depends upon the surface tension of the pore water to maintain its structure.

The reversal of the data above 1 percent amine content (i.e., decrease in both liquid limit and plastic limit) is similar to the performance of soil treated with lime. A dispersed soil treated with lime will flocculate until the optimum lime content is reached. Lime in excess of this amount will cause a partial redispersion of the soil particles accompanied by an increase in the plasticity index (1).

Figure 3 shows the plasticity index reduction due to the use of TETA and DETA alone. TETA reduces the plasticity from 19 to 6 or by 13. DETA reduces it from 19 to 9 or 10. The relative reduction is approximately proportional to the hydrogen ions offered by each curing agent. TETA offers 6 and reduces the plasticity index by 13, DETA offers 5 and reduces the plasticity index by 10 (i.e., $5/6 \cong 10/13$). The titration data in Table IV indicates that between .75 percent and 1.0 percent amine content, any additional amine remained unreacted in the soil.

Although the plasticity index reduction due to the amine alone is substantial, the amine will probably hydrolyze and decompose in time and the plasticity index will revert to the value found for the soil before treatment.

A greater reduction in the plasticity index was attained by using both amine and resin combined (See Figures 5 and 6). In this case, two major reactions transpired. The resin and part of the amine reacted by crosslinking to produce a cured epoxy, and part of the amine reacted directly with the soil.

The amount of curing agent used was well in excess of the stoichiometric amount. Evidence that there was enough amine for both reactions is shown by the titration data summarized in Tables I, II and III. The fact that unreacted amine was titrated by the hydrochloric acid indicated an excess of that amount required to satisfy both reactions. Once again, amine contents in excess of approximately 1 percent were unreacted. These results cannot be interpreted precisely because the relative extent of the competing amine-resin and amine-soil reactions cannot be determined by routine soil tests.

Figures 5 and 6 indicate the greater reduction in plasticity index that occurred when both amine and resin were used as the additive. The scatter of points on the amine-resin curve can be attributed to the fact that all amine-resin ratios were plotted. Analysis of the data in Tables II and III shows that the optimum amine content lies between .8 percent and 1.0 percent. Soil samples with amine contents of .8 percent and below showed no change in the indicator during titration whereas those in excess of 1.0 percent turned the indicator substantiating the presence of excess amine.

Figures 7 and 8 show the overall effect of 1, 2 and 3 percent amine-resin additive. Because the plasticity reduction attained with 3 percent amine-resin did not greatly exceed the performance of 1 percent, there is little practical value in using the larger amount of this relatively expensive additive.

In an effort to determine the cause of the additional decrease of the plasticity index when resin was added to the system, a wash sieve analysis was attempted as a means of indicating particle cementation. The sample was prepared by placing the dry cured chunks of treated soil, a dispersant (sodium hexametaphosphate), and distilled water into a milk shake mixer. After fifteen minutes of mixing, the contents were poured onto a #200 sieve. Despite the vigorous mixing and the presence of a dispersant, many of the original chunks remained intact. The chunks broke readily under finger pressure but since this could hardly be held constant, a meaningful wash sieve analysis was impossible to perform. The procedure did offer evidence that there was a slight cementation of particles and a very marked decrease in the surface activity of the clay particles.

Since it is not known exactly how the amine has reacted in the
-amine-soil sample, it is difficult to predict the permanence of
esulting plasticity index. It is believed that the reduction due
osslinking will remain whereas that portion of the reaction in-
ng just the soil and the amine will lose its effect in time.

TABLE I - DATA FOR 1 PERCENT AMINE-RESIN ADDITIVE

TETA

CURING AGENT/RESIN	25/100	50/100	75/100	100/100
CURING AGENT %	.20	.33	.43	.50
LIQUID LIMIT	31.7	30.6	30.3	30.4
PLASTIC LIMIT	24.2	22.5	27.2	27.2
PLASTICITY INDEX	7.5	8.1	3.1	3.2
ML HCL (FOR TITRATION)			.1	
pH	7	7.1	7.6	7.5

DETA

CURING AGENT/RESIN	25/100	50/100	75/100	100/100
CURING AGENT %	.20	.33	.43	.50
LIQUID LIMIT	40.6	34.0	35.3	34.7
PLASTIC LIMIT	24	23.4	22.7	27.0
PLASTICITY INDEX	16.6	10.6	12.6	7.7
ML HCL (FOR TITRATION)				.1
pH	7.3	7.1	7.5	8.05

TABLE II - DATA FOR 2 PERCENT AMINE-RESIN ADDITIVE

TETA

CURING AGENT/RESIN	25/100	50/100	75/100	100/100
CURING AGENT %	.40	.66	.86	1.00
LIQUID LIMIT	33.2	29.1	29.7	29.9
PLASTIC LIMIT	26.1	24.4	23.1	25.1
PLASTICITY INDEX	7.1	4.7	6.6	4.8
ML HCL (FOR TITRATION)				.5
pH	6.8	6.9	7.5	8.4

DETA

CURING AGENT/RESIN	25/100	50/100	75/100	100/100
CURING AGENT %	.40	.66	.86	1.0
LIQUID LIMIT	32.5	32.6	32.7	31.5
PLASTIC LIMIT	22.6	25.3	23.1	25.7
PLASTICITY INDEX	9.9	7.3	9.5	5.8
ML HCL (FOR TITRATION)				.3
pH	6.9	7.7	7.7	8.2

TABLE III - DATA FOR 3 PERCENT AMINE-RESIN ADDITIVE

TETA

CURING AGENT/RESIN	25/100	50/100	75/100	100/100
CURING AGENT %	.80	.99	1.29	1.50
LIQUID LIMIT	31.9	28.7	27.9	27.6
PLASTIC LIMIT	26.4	21.2	26.2	--
PLASTICITY INDEX	5.5	6.5	1.7	0
ML HCL (FOR TITRATION)		.4	.2	.6
pH	7.4	8.25	8.3	8.2

DETA

CURING AGENT/RESIN	25/100	50/100	75/100	100/100
CURING AGENT %	.80	.99	1.29	1.50
LIQUID LIMIT	35.5	31.5	31	33.3
PLASTIC LIMIT	23	23.2	27	24.5
PLASTICITY INDEX	12.5	8.3	4	8.8
ML HCL (FOR TITRATION)		.4	.5	1.71
pH	7.1	8.5	8.75	9.1

TABLE IV - DATA FOR 0-3 PERCENT AMINE ADDITIVE

TETA

CURING AGENT %	.25	.50	.75	1.0	2	3
LIQUID LIMIT	39.4	38.5	38.8	39.6	33.9	32.7
PLASTIC LIMIT	23.6	27.8	32.6	33	27.6	23.8
PLASTICITY INDEX	15.8	10.7	6.2	6.6	6.1	8.9
ML HCL (FOR TITRATION)				.9	1.4	4.7
pH				9.45	9.1	9.2

DETA

CURING AGENT %	.25	.50	.75	1.0	2	3
LIQUID LIMIT	38.3	37.8	37.1	37.5	35	31.9
PLASTIC LIMIT	23	24.2	27.5	27.8	25.3	22.3
PLASTICITY INDEX	15.3	13.6	9.6	9.7	9.7	9.6
ML HCL (FOR TITRATION)				.5	2.7	5.2
pH				9.3	9.1	9.2

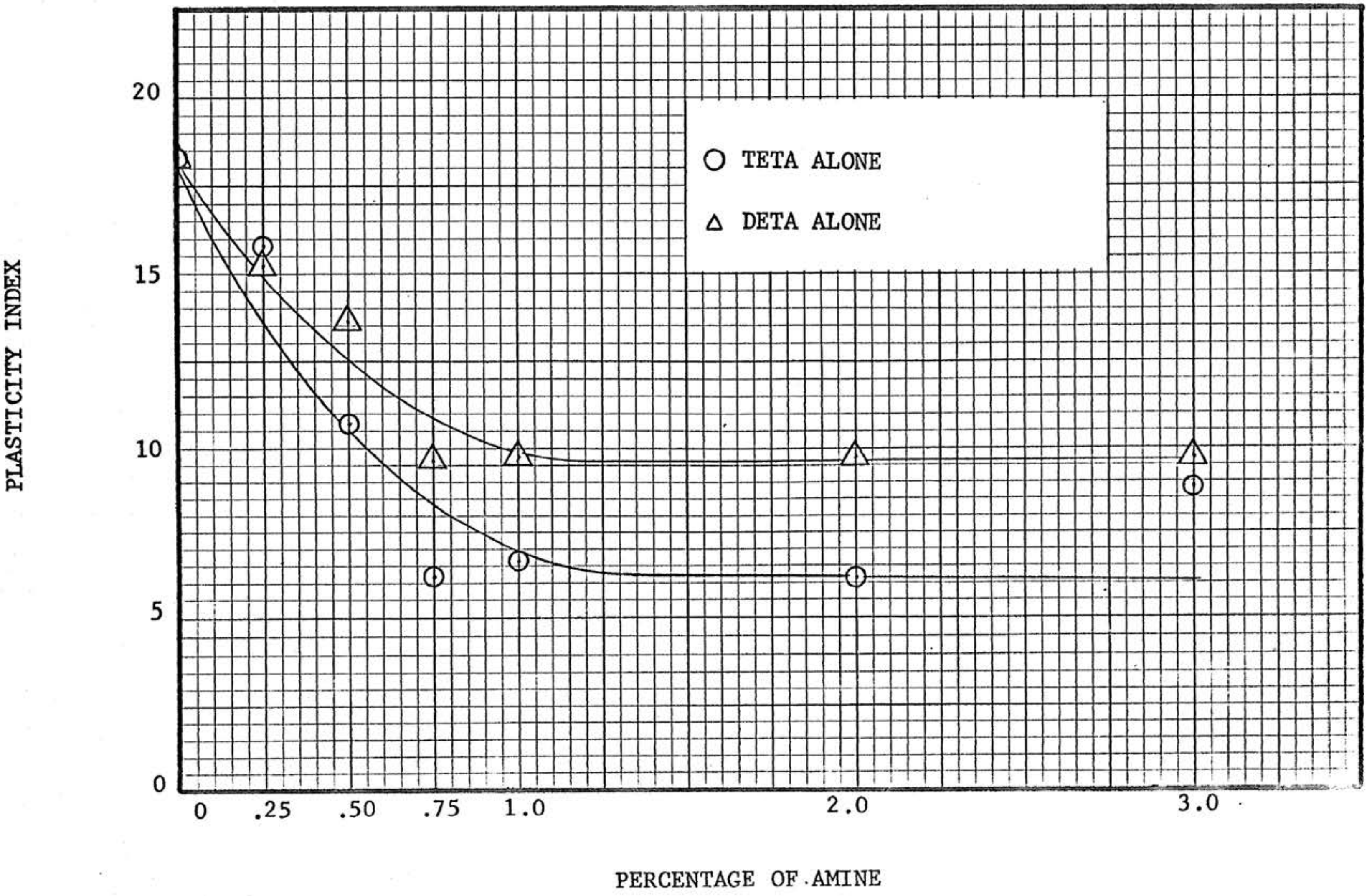


FIGURE 3. RELATION BETWEEN CURING AGENT CONTENT AND PLASTICITY INDEX

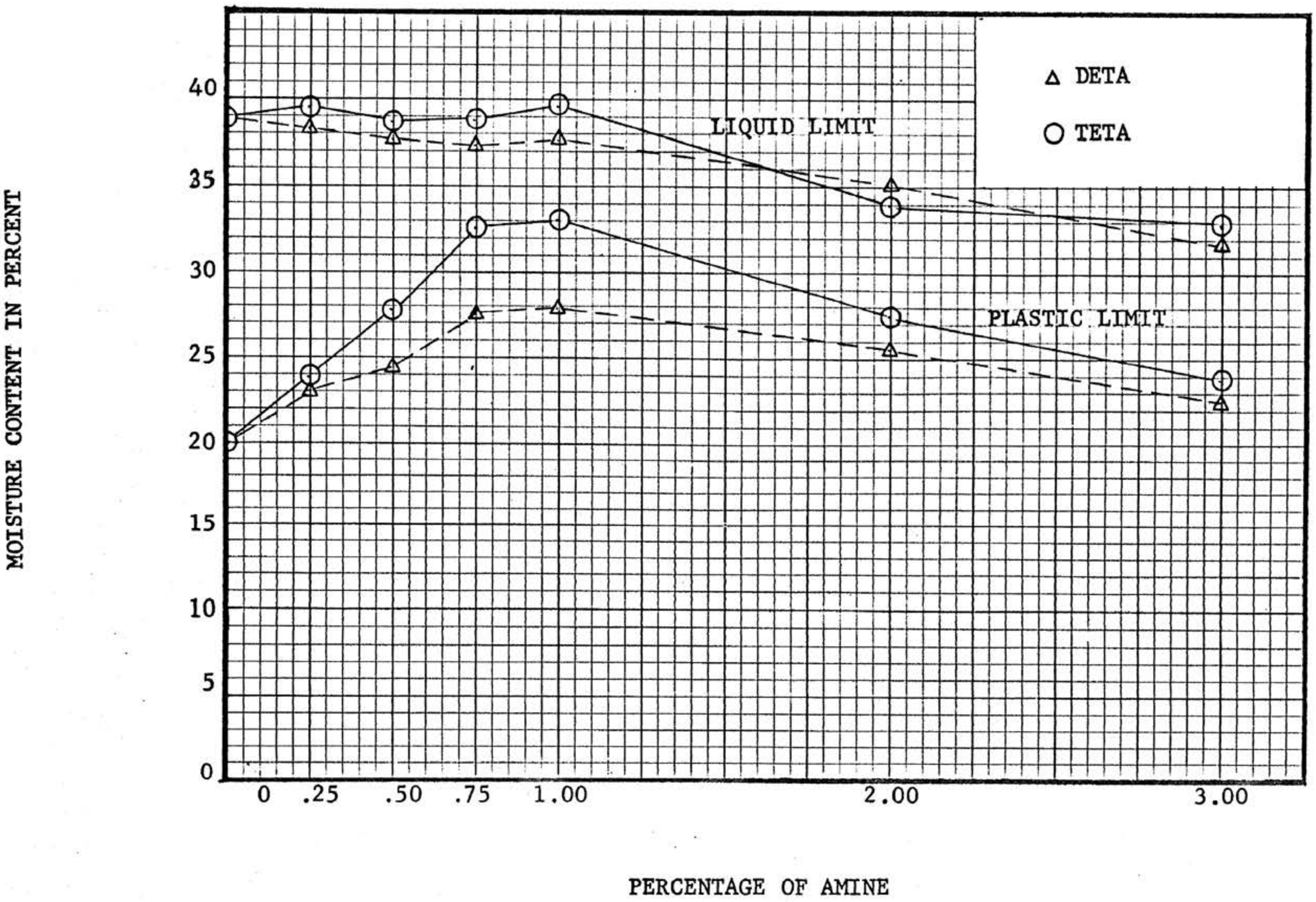


FIGURE 4. RELATION BETWEEN CURING AGENT CONTENT, PLASTIC LIMIT AND LIQUID LIMIT

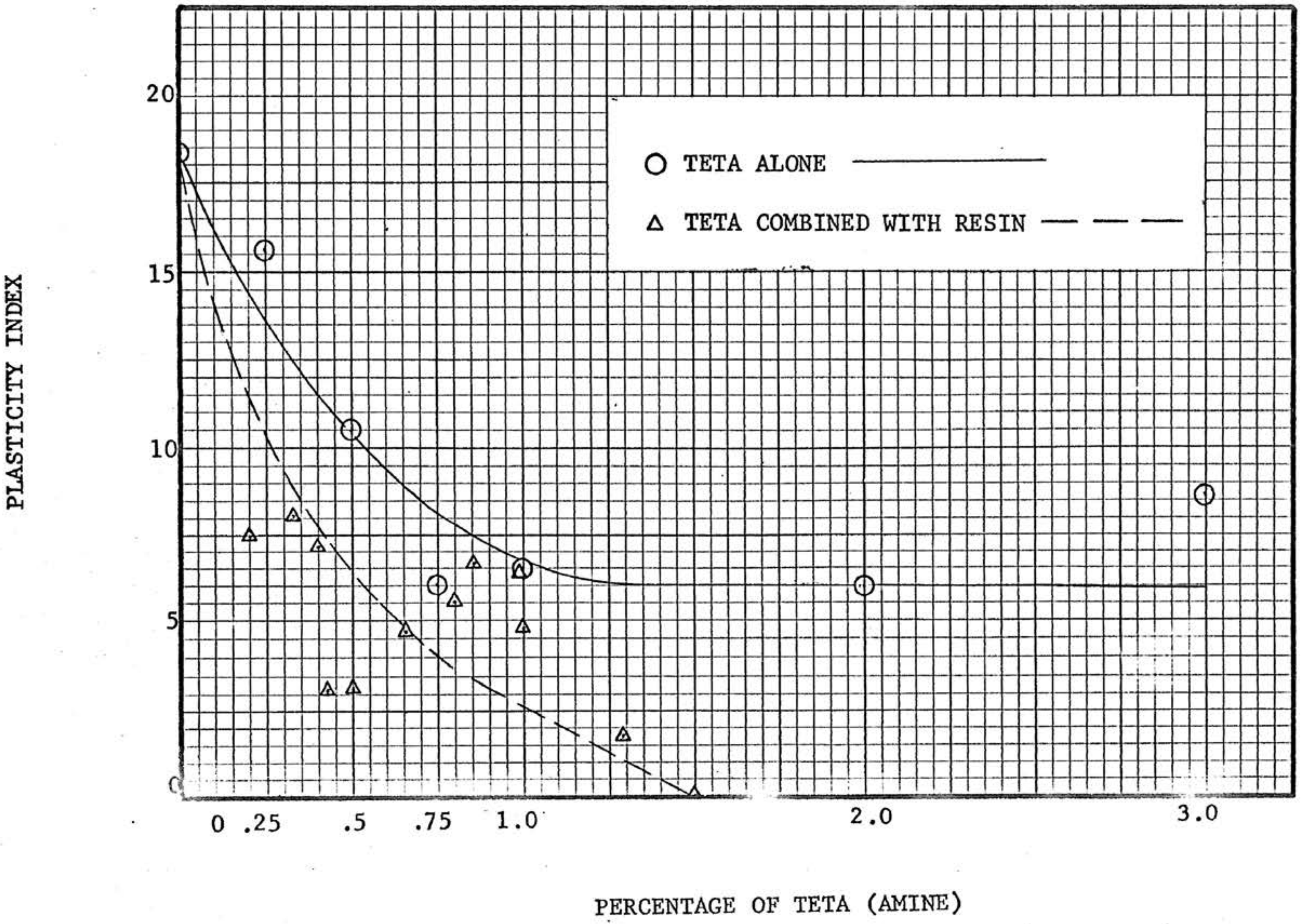


FIGURE 5. RELATION BETWEEN CURING AGENT CONTENT AND PLASTICITY INDEX

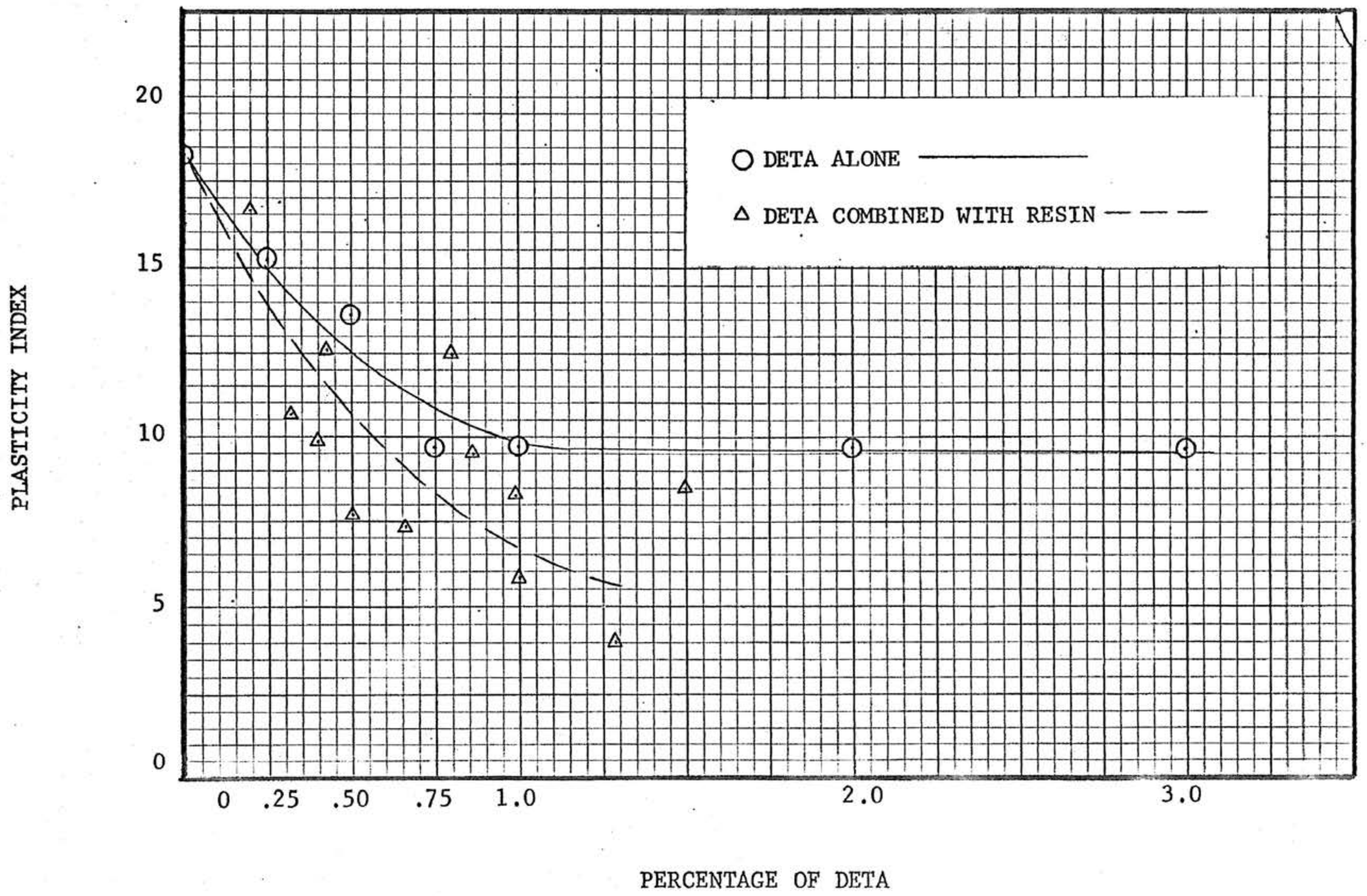


FIGURE 6. RELATION BETWEEN CURING AGENT CONTENT AND PLASTICITY INDEX

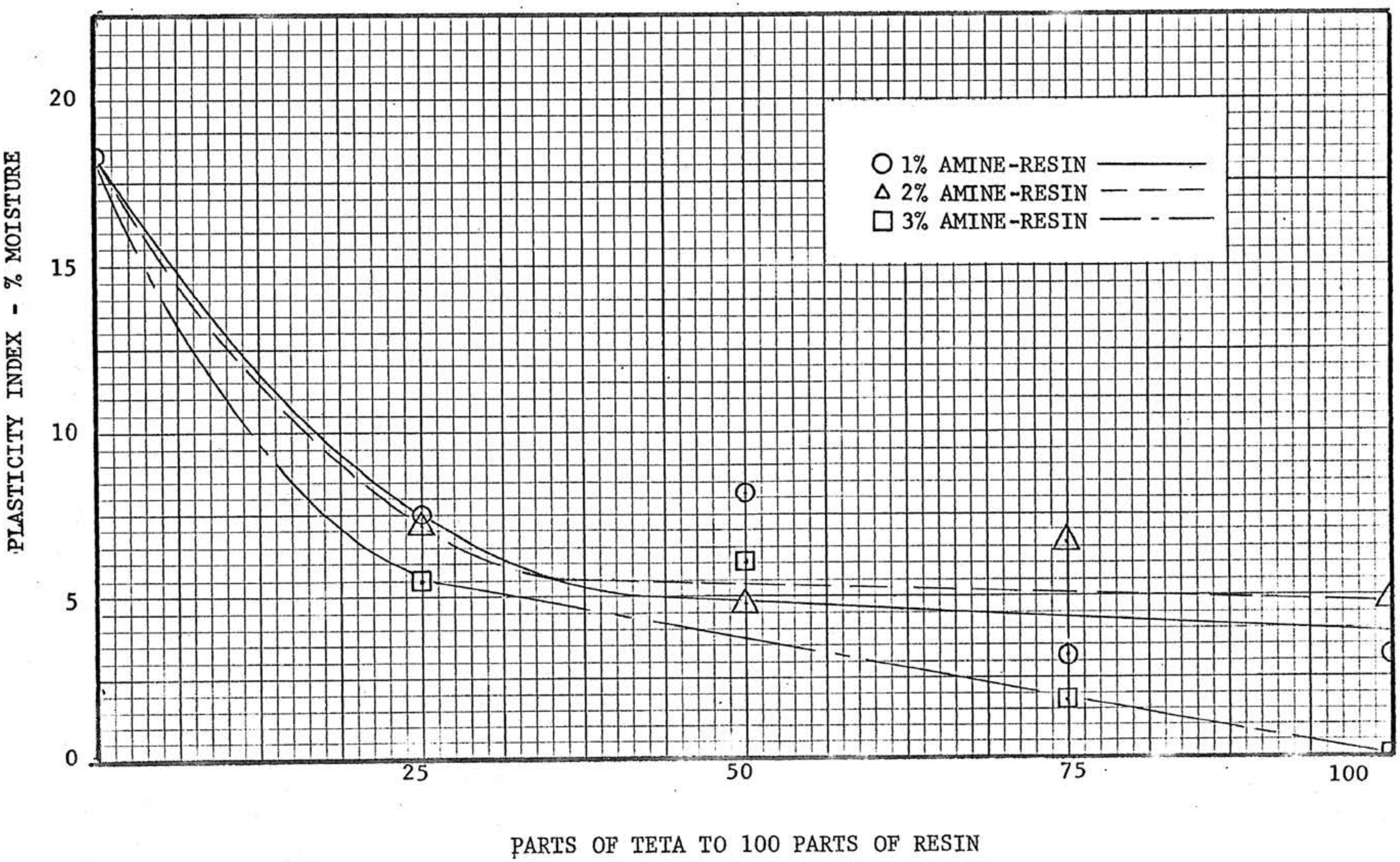


FIGURE 7. RELATION BETWEEN AMINE-RESIN MIXTURES AND PLASTICITY INDEX

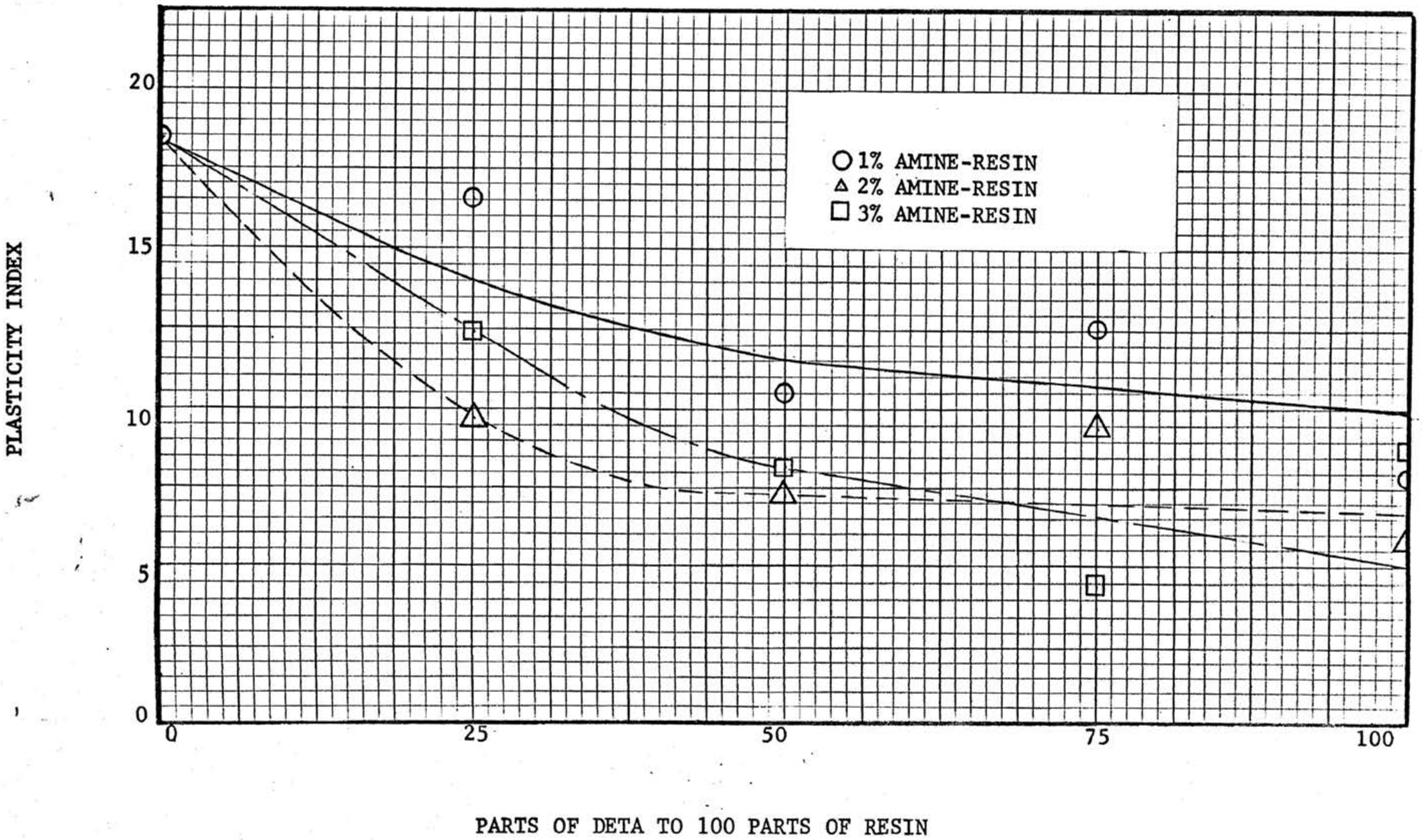


FIGURE 8. RELATION BETWEEN AMINE-RESIN MIXTURES AND PLASTICITY INDEX

IV. CONCLUSIONS AND RECOMMENDATIONS

The investigation shows conclusively that the plasticity index of a clayey soil can be reduced substantially with trace amounts of epoxy resin and curing agent (amine), or with curing agent used alone.

Explanation of the plasticity index reduction of soil treated only with the amine is quite straightforward, based on Hofmeister's lyotropic series.

On the other hand, an explanation of the proportion and extent of the competing reactions in the resin-amine-soil mixture suggests further analytically oriented research to define the reaction thoroughly.

Because of the relatively high cost of the additives used in this study, soil stabilization by epoxy resins will not be widely practiced. If and when epoxy resins and curing agents can be produced in larger quantities, thereby reducing cost, this method may prove to be highly desirable.

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VITA

A. R. Van Steenbergen was born in Melrose, Massachusetts, on April 6, 1935. He received his primary and secondary education in Boston and Newton, Massachusetts. His college education was received at Northeastern University in Boston and at the University of Missouri at Rolla. He received a Bachelor of Science Degree in Industrial Engineering from Northeastern University in 1958 and a Bachelor of Science Degree in Civil Engineering from the University of Missouri at Rolla in 1964. He has been enrolled as a graduate student in the Department of Civil Engineering at the University of Missouri at Rolla since September 1964.

The author has been a member of the United States Army, Corps of Engineers, since August 1, 1958, and presently serves that organization in the grade of Captain.

He married the former Barbara Louise Schaefer of Columbus, Ohio in September of 1960.

He has been a Registered Professional Engineer in the State of Missouri since January 1965.