

# EFFECTS OF A SYNTHETIC RESIN ON DIFFERENTIAL THERMAL ANALYSIS OF LOESS

*By*

J. B. SHEELER, R. L. HANDY, AND D. T. DAVIDSON  
Iowa State College, Ames, Iowa

## ABSTRACT

Synthetic resins offer a possible method of soil stabilization for roads; aniline-furfural is a synthetic resin showing commercial possibilities. Differential thermal analysis is a useful tool for interpreting the relation between aniline-furfural and the soils that have been stabilized by this resin.

Differential thermal curves were run on several loess soils that had been stabilized with varying amounts of aniline-furfural. The clay fraction of these soils had previously been identified as predominantly interlayered illite-montmorillonite minerals. The <2 micron clay fraction varied from 7.4 to 37.0 percent. The thermal curves showed characteristic exothermic organic reactions in the treated soils and relationships were found between the thermal reactions, the percent aniline-furfural, and the percent clay.

Double peaks were observed on the curves of all soils containing 2 percent or more of aniline-furfural. The area under the organic double peaks was found to be a function of the percent aniline-furfural. The double peak is believed to be caused by initial burning of readily available aniline-furfural followed by final burning of the remaining aniline-furfural. The release of the resin responsible for the second peak may be due to a breakdown of the clay crystal structure at about 550°C. This indicates a close association of the resin and the clay minerals. The foregoing statement is further strengthened by a linear correlation of distance between peaks and the amount of clay present. Higher aniline-furfural contents increase the area under the second peak; this increase indicates that a larger amount of the resin is being utilized in cementation of grains and is reflected by the mechanical strength of stabilized soil specimens.

## INTRODUCTION

Aniline and furfural are organic chemicals that polymerize on contact to form a resin known as aniline-furfural resin; organic cations are intermediate products in the resinification reaction. The most superior resin is produced with a ratio of 2 mols of aniline to 1 mol of furfural. Soil may be stabilized by mixing with the appropriate ratio of aniline and furfural and enough water to produce maximum density. The mixture is then compacted to maximum density and allowed an adequate curing period before testing.

Furfural is produced from agricultural by-products such as oat hulls, cottonseed hulls, or ground corncobs by pressure cooking with dilute acid. Aniline is manufactured by the reduction of nitrobenzene, ammonolysis of chlorobenzene, or vapor-phase hydrogenation of nitrobenzene. The method of reduction of nitrobenzene is by far the most widely used.

Secondary road construction in Iowa is dependent mainly on natural rock or gravel deposits to furnish the material for surface and base courses. These deposits are being rapidly depleted and some sections are now suffering severe shortages. One solution to this problem is to treat or process locally occurring

soils and soil materials with chemicals or additives to produce a material suitable for the construction of all-weather roads. The Iowa Engineering Experiment Station is investigating numerous treatments of various Iowa soils and soil materials in an effort to solve or alleviate this problem. Because of the widespread distribution of Wisconsin loess in Iowa, this material has received considerable attention as to its properties and stabilization possibilities.

Aniline-furfural resin has been investigated as a loess-stabilizing material in considerable detail. Differential thermal curves have been run on aniline-furfural stabilized loess as an aid in the investigation and determination of the mechanism responsible for the success encountered when this synthetic resin is used as a loess-stabilizing agent.

### DESCRIPTION OF SOILS

The soils used throughout this study were obtained from the loess deposits in southwestern Iowa. Davidson and Handy (1952) have shown that this loess is a fine-textured soil material consisting predominantly of particles of silt and clay. The mineralogical nature of this early Wisconsin loess seems to be quite uniform. Organic matter and soluble sulfate contents are very low or nonexistent. The principal mineralogical variables in the loess are the magnitude of carbonate and clay content. The minus 5 micron material is very similar throughout and consists mainly of clay minerals which are thought to exist as a randomly interstratified mixture of montmorillonite and illite. X-ray diffraction data indicate an increase in the montmorillonite:illite ratio with increasing clay content in the loess. Microscopic examination has shown that the clay occurs mainly as coatings on larger grains.

Since the main variables in the loess appear to be the amounts of clay and carbonates, with clay the dominant variable, six samples were chosen as representative of the range of these variables. The clay content ranged from 7.4 to 37.0 percent <2 micron clay; the carbonate content is about 7 percent in two samples and 1 percent in the remaining four.

### TREATMENT OF SOIL WITH ANILINE-FURFURAL

Each sample of soil was mixed with varying amounts of aniline and furfural in a 2:1 molar ratio and compacted to maximum density in molds 2 inches in diameter by 2 inches high. These 2 inch by 2 inch samples were then extruded from the mold and allowed to cure at indoor atmospheric conditions for ten days. During this curing period the aniline and furfural undergo a chemical union to form a resin which stabilizes the soil mass. The resulting samples were then subjected to various strength and weathering tests. The materials used to obtain the differential thermal curves analysed in this paper were salvaged from samples that had been subjected to unconfined compression testing. Because the salvaged material is ground with a mortar and pestle before the thermal analysis, the unconfined compression testing with its resultant

crushing of the sample does not influence the final results. The resin content of the samples analyzed ranged from 0 to 11 percent of the oven-dry weight of the soil.

### DIFFERENTIAL THERMAL ANALYSIS

The samples used to obtain the differential thermal curves shown in Figures 1, 2, 3, and 4 were obtained by grinding the salvaged specimens to pass a no. 40 sieve. The resulting material was poured into the sample well which was three-eighths inch in diameter and three-eighths inch deep. The sample was then packed by finger pressure and all excess material was removed, leaving the sample well completely full. Previous studies have shown the density of this stabilized soil material to be quite uniform. The above procedure should therefore insure a constant amount of sample for each run.

The differential thermal curves were run with a heating rate of 10°C per minute and a chart speed of 6 inches per hour. A linear heating curve was maintained and recorded on a Brown strip-chart recording potentiometer. The differential temperature curve was recorded on a similar instrument that was

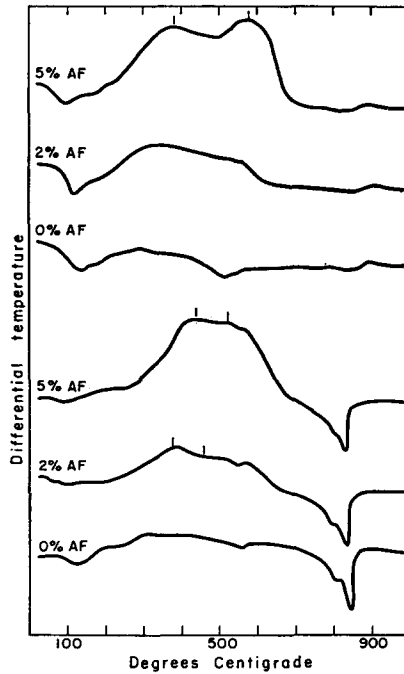


FIGURE 1. — Differential thermal curves from loess samples stabilized with the percentages of aniline-furfural resin indicated at the origin of the curves. The top three curves are from samples containing 26.3 percent <2 micron clay; the lower three curves are from samples containing 7.4 percent <2 micron clay.

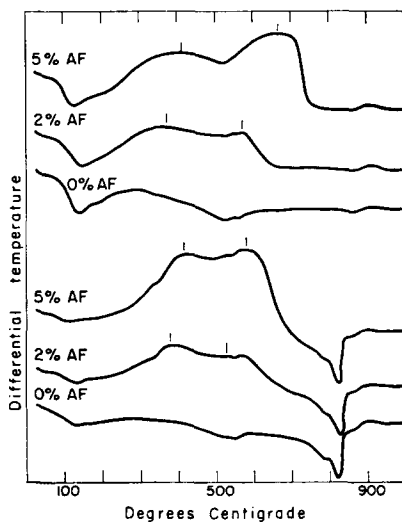


FIGURE 2. — Differential thermal curves from loess samples stabilized with the percentages of aniline-furfural resin indicated at the origin of the curves. The top three curves are from samples containing 37.0 percent  $<2$  micron clay; the lower three curves are from samples containing 21.7 percent  $<2$  micron clay.

synchronized with the temperature chart. The samples were heated from room temperature through  $1040^{\circ}\text{C}$ .

All differential temperature curves obtained from samples containing 2 or more percent resin exhibited a double peaked exothermic reaction similar to that reported by Allaway (1948), the first peak occurring near  $400^{\circ}$  to  $450^{\circ}\text{C}$  and the second peak following a clay reaction that occurs at about  $500^{\circ}\text{C}$ .

The time lapse between peaks was determined for the samples containing 2 percent resin and for the samples containing 5 percent resin. The peak of each exothermic reaction is defined as the maximum point of differential temperature as shown in Figure 5.

The area under the organic exotherms was divided into two parts by a vertical line drawn from the minimum differential temperature shown on the  $500^{\circ}\text{C}$  clay endotherm. These areas were further bounded by a line drawn from the point of intersection of the thermal curve and the  $240^{\circ}\text{C}$  line to the level portion of the new zero line at about  $900^{\circ}\text{C}$ . This line is made necessary because some drift of the zero line occurs and it has been assumed that this drift is linear with temperature. The points and areas mentioned above are illustrated in Figure 5. The  $240^{\circ}\text{C}$  line was used as a datum because the organic exotherms seem to start at this temperature.

The areas described above were determined with a planimeter for the soils containing 18 and 26 percent  $<2$  micron clay. An excellent discussion and analytic proof of quantitative relations between the area under a peak and the

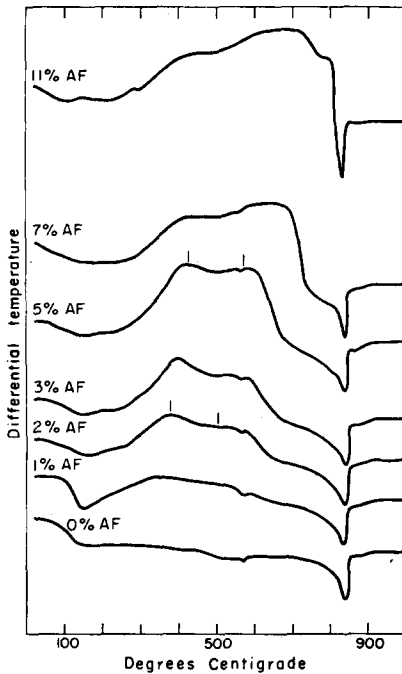


FIGURE 3.—Differential thermal curves from loess samples containing 17.8 percent  $<2$  micron clay and stabilized with the percentages of aniline-furfural resin indicated at the origin of the curves.

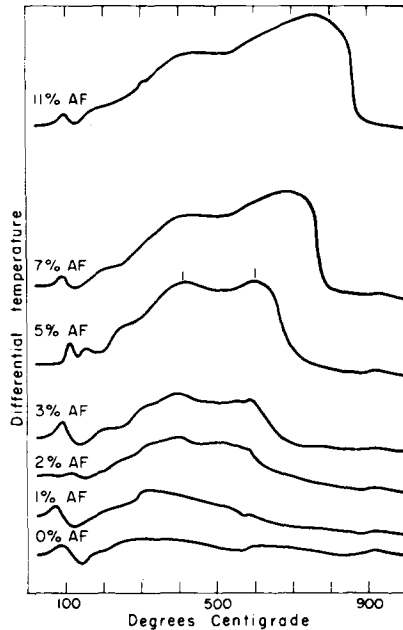


FIGURE 4.—Differential thermal curves from loess samples containing 26.3 percent  $<2$  micron clay and stabilized with the percentages of aniline-furfural resin indicated at the origin of the curves.

amount of reacting material present is given by Kerr, Kulp, and Hamilton (1949).

## RESULTS AND INTERPRETATIONS

Plots of time between peaks versus the amount of  $<2$  micron clay in samples containing 2 percent resin and 5 percent resin are shown in Figure 6. Both plots show a linear correlation between these two variables, the curve for the 5 percent resin content having a steeper slope than the curve for the 2 percent resin content. This indicates that the rate of resin combustion is controlled and retarded by the degree of resin-clay association. The more clay present the more resin held in the resin-clay bond. The more resin present the higher the degree of association.

Some of the differential thermal curves did not exhibit a clear maximum peak and therefore were not included in the data. This was particularly so in the samples that had been treated with the lower percentages of resin. Examination of the differential thermal curves indicates that a treatment of about 4

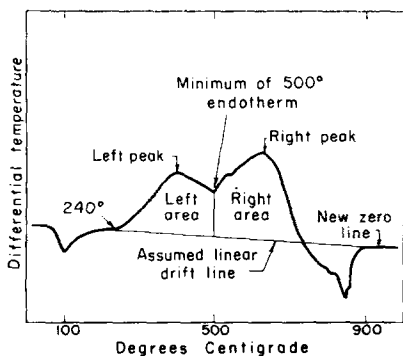


FIGURE 5.—A hypothetical differential thermal curve illustrating the definition of a peak and the method used in obtaining the areas under the peaks.

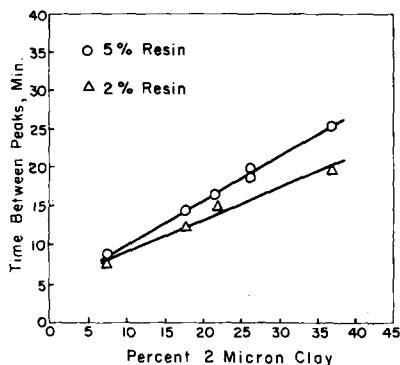


FIGURE 6.—Time between peaks plotted against <2 micron clay content for resin contents of 2 and 5 percent.

percent resin would produce exothermic reactions having the most clearly defined double peaks.

The formation of aggregate particles is promoted by the addition of aniline and furfural during mixing. The aggregates remain together after compaction and curing as evidenced by studies of strength and moisture absorption, and by microscopic examination. These studies further indicate that the amount of aggregation reaches a maximum in the resin content range of 3 to 5 percent.

The areas beneath the left peaks and the areas beneath the right peaks were plotted against the percentage of resin for two different soils (Fig. 7). Both plots show a tendency for the area under the left peak to reach a maximum value at about 5 percent resin content and to remain nearly constant thereafter. The constant area under the left peak indicates a constant amount of resin involved according to Kerr's thermodynamic treatment of quantitative differential thermal analysis. Evidently the rate of resin consumption is limited by some factor. This factor can not be the oxygen supply, since the rate of combustion exhibited by the right peak is obviously greater. Exposed surface area appears to be a possibility and is thought to be the answer because it integrates well with aggregation evidence. Once maximum aggregation is reached, any additional resin serves mainly to fill voids within the aggregate particles. The actual volume of the aggregate is increased only slightly with each increase in resin content. Since the rate of combustion is governed by the amount of surface exposed it appears that the size of the left peak is controlled by the amount of aggregation and possibly somewhat by the amount of free resin that is not associated with the clay.

The areas under the right peaks, also plotted against resin content in Figure 7, show a linear relation between these two variables at resin contents of more than 3 percent. This peak is thought to be caused by adsorbed organic cations and by the resin that binds the soil particles together into aggregates. The

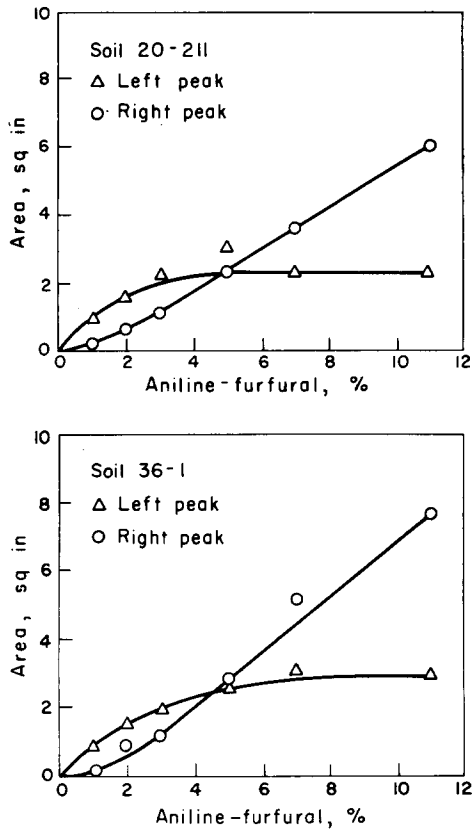


FIGURE 7. — Areas under the left and right peaks plotted against the aniline-furfural content. Soil 20-2 II contained 17.8 percent  $<2$  micron clay, and soil 36-1 contained 26.3 percent  $<2$  micron clay.

higher the resin content the higher the amount of resin that is retained within the aggregates. Obviously, the amount of resin that can be retained within an aggregate particle is limited by the amount of space available. Evidently this point has not been passed with the highest percentage of resin employed in this study.

During grinding the weakest and thinnest parts of the resin matrix are broken and exposed, the breaks occurring between aggregate particles. These surfaces are the first material to be burned, giving rise to the left exothermic peak. The second peak would then be due to the resin remaining within an aggregate of particles that are bonded together by the resin-clay association. This organic matter would become exposed only after the breakdown of the clay mineral structure occurs. Such a breakdown would destroy the resin-clay bond and in doing so the aggregate itself would be mechanically weakened, thus exposing the resin.

Addition of the ordinates of the two curves in Figure 7 produces a nearly linear curve. This lends support to the analytic proof offered by Kerr, Kulp, and Hamilton (1949).

The occurrence of the clay endotherm further sharpens the double peak by virtue of its superposition on the exothermic reaction. Conversely, a weak endotherm is exaggerated by the exothermic peaks as can be seen by comparison of the three curves at the bottom of Figure 1, which represent a loess sample containing only 7.4 percent <2 micron clay.

#### ACKNOWLEDGMENT

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#### REFERENCES

- Allaway, W. H., 1948, Differential thermal analysis of clays treated with organic cations as an aid in the study of soil colloids: *Soil Sci. Soc. Am. Proc.* v. 13, p. 183-188.
- Davidson, D. T., and Handy, R. L., 1952, Property variations in the Peorian loess of southwestern Iowa: *Iowa Academy of Science Proc.*, v. 59, p. 248-265.
- Kerr, P. F., Kulp, J. L., and Hamilton, P. K., 1949, Differential thermal analyses of reference clay mineral specimens: American Petroleum Institute Project 49, Prelim. Rept. no. 3.