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Coal Acids - An Intermediate For Thermosetting Resins

By

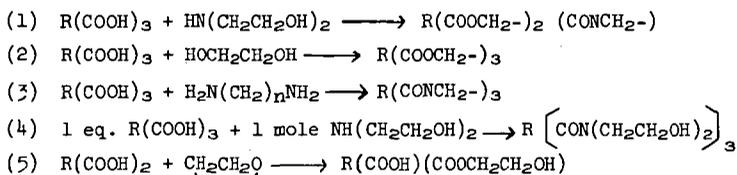
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INTRODUCTION:

Gaseous oxygen oxidation of an alkaline slurry of bituminous coal yields a mixture of water soluble aromatic polycarboxylic acids (1). These coal acids have been shown to have three principle aromatic ring systems, namely benzene, naphthalene and diphenyl (2). The mixture is strongly acidic and has an average functionality of approximately three.

The coal acids afford an interesting and relatively inexpensive raw material. One specific use of these acids is in the preparation of thermosetting resins. The large markets for resins of this type provided an interesting field of investigation and efforts to develop these resins are outlined in this paper.

Coal acids can be reacted with an alkanolamine, alkylene oxide, polyhydroxyl compound or polyamine to give thermosetting resins. Variation of reactants, the equivalents used or the reaction conditions allows a wide spectrum of resins with varying properties. The polyamide, polyester or combination of functional groups possible in these resins are shown in examples 1-5. In examples 1, 2 or 3 an equivalent of hydroxyl or amine reactant



is used for each carboxylic acid equivalent, while in example 4 one mole of diethanol-amine is used per equivalent of acid group. The latter resin will have free hydroxyl groups which could then be crosslinked. Use of a large excess of a glycol reactant with the coal acids also yields a resin with free hydroxyl groups. The preparation of a partially reacted ester with free carboxylic acid and hydroxyl groups is shown in example 5. The resultant water soluble resin intermediate gives a crosslinked structure when cured at elevated temperatures.

A. Preparation and Chemistry of the Resins

Alkanolamine, Polyhydroxyl and Polyamine Resins

The mixture of aromatic polycarboxylic acids (coal acids) obtained from the Coal Research Laboratory of the Carnegie Institute of Technology in Pittsburgh was used in the preparation of some of the resins. The average molecular and equivalent weights are 270 and 82 respectively giving an average carboxylic acid functionality of 3.3. Many of the later resins were prepared from coal acids made at the Dow Chemical Company. These coal acids were shown by equivalent and molecular weight determinations to be similar to the material obtained from the Carnegie Institute of Technology.

A novel and useful feature of these resins is that a mere physical mixture of the coal acids and other reactant in water may be applied directly to the substrate to be bonded. This method of application eliminates the hazard and expense of

organic solvents in commercial applications. The resin adduct in a concentration range of 50-80% solids gives a water solution of workable viscosity and good film forming properties.

A partially cured but still water soluble coal acid resin was prepared from the coal acids and monoethanolamine by heating equivalent amounts of the reactants at 170°C. for 3 hours. Approximately 85% of the water of esterification slowly distilled off giving on cooling a water soluble solid. Titration of this material revealed the presence of nearly all the original amine salt groups. Use of a di or trialkanolamine however yields water insoluble products because of excessive crosslinking of the hydroxyl group.

Another partially cured, but still water soluble resin can be prepared from the coal acids and pentaerythritol. A suspension of an equivalent of pentaerythritol in a 70% solids solution of one equivalent of coal acids in water was stirred and heated at reflux for 3 hours. The resultant solution on titration showed 27% esterification of the pentaerythritol, while after 24 hours of reflux the esterification approaches an equilibrium value of 40%. The partially advanced resin is a viscous solution which does not exhibit any precipitation on standing for prolonged periods.

Alkylene Oxide Derived Resins

Ethylene, propylene and butylene oxide have been reacted with the coal acids in a dioxane media to produce partially reacted esters containing carboxylic acid and hydroxyl groups. These products, which are water soluble in concentrated solutions, can be cured to give a thermosetting resin. The resin of primary interest involves the reaction of one mole of ethylene oxide with two equivalents of coal acids as shown in example 5.

The alkylene oxide addition is generally allowed to proceed until one half of the carboxylic acid groups have reacted giving a resin intermediate which on final cure has no reactive groups. Wide deviation from the 50-50 acid hydroxyl group ratio may give a thermoplastic resin on final cure.

Ethylene oxide adducts with equivalent weights in the range of 162 to 328 have been prepared as have propylene oxide adducts with equivalent weights of 170-440. Reaction with butylene oxide is slower and required the addition of a small amount of sulfuric acid and additional heating at 60°C. to give an adduct with an equivalent weight of 223.

Resin Compatibility with Phenol - Formaldehyde Resins

Preliminary work has shown that various coal acid resin adducts are compatible with the "A or B stage" water borne phenol - formaldehyde resins. However the amine salt character of the alkanolamine or polyamine - coal acid resins limit their compatibility with alcohol borne phenol - formaldehyde resins.

Laboratory investigation has indicated that an actual reaction can occur between the coal acids and the phenol - formaldehyde resin.

Various amounts of coal acids were mixed with both "A" and "B" stage phenol - formaldehyde resins and the mixtures cured. The cured resin mixtures were then titrated in order to determine the amounts of the coal acids that had been incorporated into the cured resin structure. It was found that the "A stage" resin could combine with approximately 43% of its weight of coal acids but the "B stage" resin only 7% of its weight. This can be explained by the fact that the "A stage" resin contains a much larger proportion of free methylol groups than does the "B stage" resin.

B. Reaction Rate Studies

Reaction rate studies of the alkanolamine - coal acid resin adducts have afforded information concerning the relative rates of ester formation as compared with amide - imide formation. The usual methods for kinetic studies are useless in this case because of the highly crosslinked and insoluble nature of the coal acid resins. The most satisfactory solution to the problem was to cure weighed samples of the resin adduct on squares of aluminum foil which were floated on the surface of a Wood's metal bath controlled at a fixed temperature. The resin samples were prepared from a mixture of 1:1 equivalent of alkanolamine - coal acids containing 10% water. The sample after cure was digested in a methanol - water solution and titrated with 1N sodium hydroxide. A plot of pH vs. milliequivalents of alkali revealed two points of inflections, one occurring at approximately pH 7 and indicating free carboxylic acid group and the second inflection point at pH 9.5-10.5 which corresponded to the amine salt component.

Samples were run for various time intervals and the milliequivalents of unreacted carboxylic acid groups and/or amine salt groups plotted vs. the cure time in minutes. The semilogarithmic plot approximated a straight line suggesting a first order reaction. This behavior is reasonable, since both reactants are combined into one molecular species by means of the amine salt formation.

A typical plot of an alkanolamine - coal acids reaction is shown in Figure 1. In this case samples of a 1:1 equivalents formulation of the diethanolamine - coal acid resin were cured at 265°C. Line A shows the disappearance of the combined free carboxylic acid and amine salt groups, line B the esterification rate while line C is the rate of formation of the amide or imide. The reaction rate constants and half lives of the mono, di and triethanolamine - coal acid resin reactions are shown in Table I. The slower rates exhibited by the di and triethanolamine resins are probably due to steric hinderance. Use of an acidic catalyst gave the expected reaction rate increase.

Cure rates of the diethanolamine - coal acid resin were determined for temperatures in the range of 240-300°C. to give the Arrhenius plot shown in Figure 2. The slope of the plot is only slight in this temperature range while determinations at 150 and 210°C. gave rate constants far below this range. These lower rate constants may be partially due to a lower heating efficiency of the experimental setup at these temperatures or perhaps indicate a reaction rate threshold effect.

Preliminary work has shown that reaction rates of the coal acid - glycol resins can also be determined provided a lower temperature, e.g. 150°C., is used in order to reduce the evaporation losses of the glycol. Figure 3 is a plot of the reciprocal of the square of the carboxylic acid concentration vs. time as obtained with a coal acid - diethylene glycol resin system. Since the reactants have the same initial concentration, the resultant straight line plot indicates a third order reaction. This is in accord with the mechanism of an acid catalyzed esterification. The catalyzing acid in this reaction is the coal acids because of the strong acidic nature.

A rate study of the coal acid - pentaerythritol resin adduct has proven interesting since the results indicate a first order reaction similar to the alkanolamine resins. The reactants were heated in water to give a partially esterified resin which on titration showed 18% advancement. Samples of the 75% solution were then cured in the normal manner at 230°C. Use of the titration procedure gave a plot shown in Figure 4. A first order reaction is reasonable if one considers that a large portion of the partially cured resin adduct is in the form of a molecular species having both acid and hydroxyl groups. Thus the reaction in this study would be primarily an intramolecular polycondensation and first order. Calculation

of the first order reaction rate constant for this reaction gives a value of 0.175 minutes⁻¹ and a half life of 3.95 minutes respectively.

Saponification of Coal Acid Resins

A brief look at the saponification rates of some of the coal acid polyesters may be of interest at this point. The completely cured resin (225°C. for 2 hours) ground to less than 250 mesh was suspended in N/10 sodium hydroxide. The suspension was stirred at room temperature and portions removed at intervals for titration. The saponification rates of the diethanolamine, ethylene glycol and pentaerythritol resins of the coal acids are shown in Figure 5. The lower saponification rates of the diethanolamine and pentaerythritol resins can be explained by steric hinderance. Saponification of the pentaerythritol resin by several different concentrations of sodium hydroxide shows that the rate and extent of degradation is proportional to the alkali concentration.

C. Physical Properties of Coal Acid Resins

1. Physical Strength

Sand briquettes were used as the test media in determining the physical strength of the coal acid resins. The one inch thick sand briquettes were of the figure eight shape and identical to the form adopted by the A.S.T.M. for evaluation of foundry molding sands. Table II lists the tensile strengths of the various resin bonded sand briquettes. All the resins were physical mixtures of one equivalent coal acids and one equivalent reactant in water unless otherwise stated.

The resins in order of decreasing strength are the ethylene oxide adduct, pentaerythritol, glycol and alkanolamine adducts. The alkanolamine type resins can be considerably overcured without impairing their strength, while a glycol resin bonded briquette overcured for 5 minutes at 260°C. suffers a strength loss of some 20%.

2. Heat Stability of Cured Coal Acid Resins

Investigation of the coal acid resins as a glass fiber binder prompted a study of the resin's heat stability. Briefly, the method of test consisted of suspending a powdered sample of the cured resin in a wire screen holder placed in a vertical furnace. A thermocouple placed in the sample continuously measured the temperature of the sample as the furnace temperature was gradually increased and the resin started to burn. The slope of the combustion temperature curve between 700 and 1100°F. was used to express the rate of resin combustibility. The reciprocal slope ($\Delta \text{ temp.} / \Delta \text{ time}$) was used in order to obtain numbers greater than one. If no resin combustion takes place under the conditions used the resin sample temperature will not exceed 700°F. Therefore, the temperature line between 700 and 1100°F. would be due to the resin heat of combustion.

A second heat stability test applied to our resins determined the critical temperature at which the resin would completely burn without added heat. The overall heat stability of the particular resin was shown by combining the slope factor and critical temperature into the expression $\frac{\Delta \text{ temp.} / \Delta \text{ time}}{\text{critical temp.}}$. Some of our combustibility data from this slope method are given in Table III.

The resins in order of decreasing heat stability are diethylene-triamine, diethanolamine, ethylene glycol adduct and phenol-formaldehyde resins. The heat stability of the coal acid - polyamine resin is similar to some melamine type resins.

CONCLUSIONS:

The coal acids undergo polycondensation reactions with alkanolamines, polyhydroxyl or polyamine reactants to give thermosetting resins. Proper choice of reactants, reactant ratios and reaction conditions allows the preparation of a large number of resins with varying properties. The resin adducts may be simple mixtures of the reactants in water or a partially reacted resin which is still water soluble.

The cure process of the various resins can be followed by titration of the still unreacted carboxylic acid or amine salt groups. Thus a method is available for the evaluation of various reactants and conditions in the preparation of the coal acid resins.

Physical properties of these resins that have been studied include their strength and heat stability. The resins in order of decreasing strength are the ethylene oxide adduct, pentaerythritol, glycol and alkanolamine - coal acid resins. Many of the coal acid resins have physical strengths sufficient to allow their use as resin binders. The heat stability of several coal acid resins have been found to be superior to a typical "A stage" phenol - formaldehyde resin.

REFERENCES:

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TABLE I

CURE RATES OF ETHANOLAMINE - COAL ACID RESINS AT 265°C.

| Resin | Total | | Ester | | Amide/Imide | |
|---|---------------------|-----------------------|---------------------|-----------------------|---------------------|-----------------------|
| | k min ⁻¹ | t _{1/2} min. | k min ⁻¹ | t _{1/2} min. | k min ⁻¹ | t _{1/2} min. |
| Monoethanolamine | 1.22 | 0.57 | 1.67 | 0.42 | 0.82 | 0.85 |
| Diethanolamine | 0.68 | 1.02 | 0.73 | 0.95 | 0.62 | 1.12 |
| Triethanolamine | 0.41 | 1.68 | 0.46 | 1.50 | 0.28 | 2.44 |
| Diethanolamine With 5% poly H ₃ PO ₄ | 0.87 | 0.80 | 0.96 | 0.72 | 0.72 | 0.98 |

TABLE II

TENSILE STRENGTHS OF COAL ACID RESIN BONDED SAND BRIQUETTES

| <u>Reactant</u> (6% green solids) | <u>Cure</u> <u>Conditions</u> | <u>Tensile</u> <u>Strength, psi.</u> |
|--------------------------------------|----------------------------------|---|
| Monoethanolamine | 15 min./260°C. | 128 psi. |
| Diethanolamine | " " | 458 |
| Triethanolamine | " " | 302 |
| Ethylene glycol (1) | " " | 562 |
| Diethylene glycol | " " | 690 |
| Propylene glycol | 10 min./260°C. | 464 |
| Dipropylene glycol | 22 min./260°C. | 494 |
| Triethylene glycol | 18 min./260°C. | 580 |
| Ethylene oxide (2)(3) | 40 min./225°C. | 830 |
| Pentaerythritol (4) | 45 min./250°C. | 738 |

- Footnotes: (1) 5.5% resin solids
 (2) Coal acid - ethylene oxide adduct at approximately 50% reaction.
 (3) Thermoplastic after 30 min. cure
 (4) Resin composed of 1 eq. coal acid and 0.9 eq. of pentaerythritol and reacted to 16% esterification.

TABLE III

COMBUSTIBILITY RATES OF CURED RESINS

| Resin or Coal Acid Reactant | Temp. | Critical | Slope |
|-----------------------------------|-------------------------------|-----------|--|
| | Time (°F. min ⁻¹) | Temp. °F. | Critical Temp. x 10 ³ min ⁻¹ |
| "B stage" phenol-formaldehyde | 200 | 400°F. | 500 |
| 50% Diethanolamine | 80 | 680°F. | 117 |
| 50% "B stage" phenol-formaldehyde | | | |
| Diethanolamine | 66.5 | 700°F. | 95 |
| Diethylene-triamine | 16-20 | 690°F. | 23 |
| Ethylene glycol | 150 | 625°F. | 240 |

Figure 1

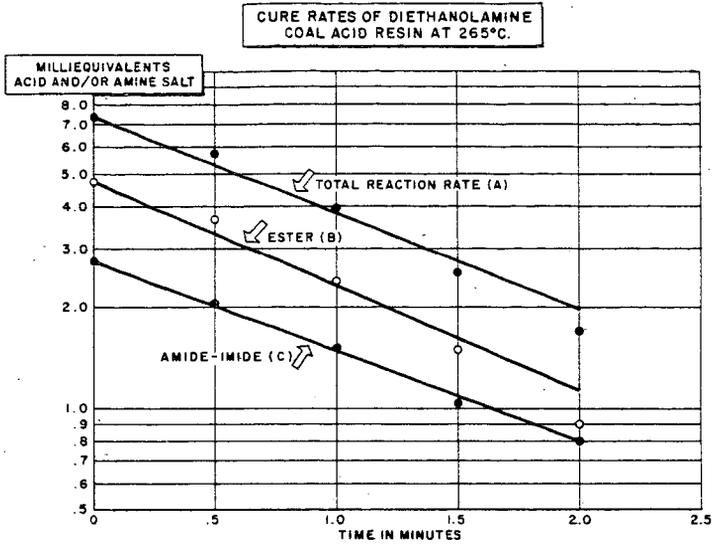


Figure 2

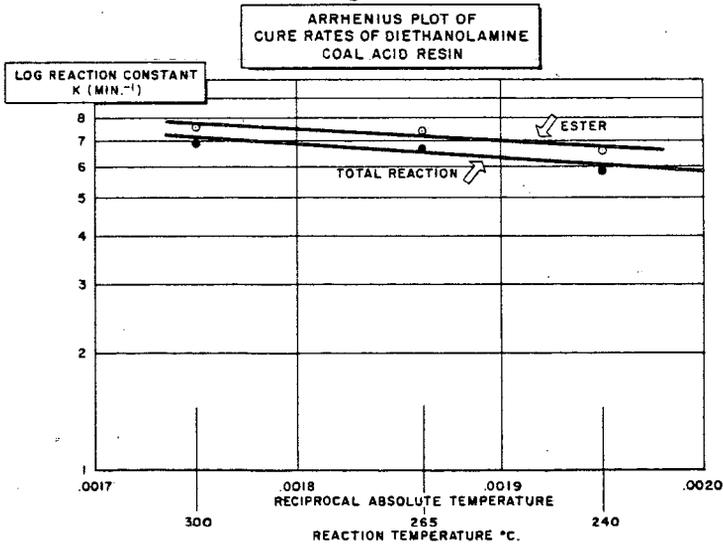


Figure 3

CURE RATE OF COAL ACIDS
DIETHYLENE GLYCOL RESIN AT 150°C.

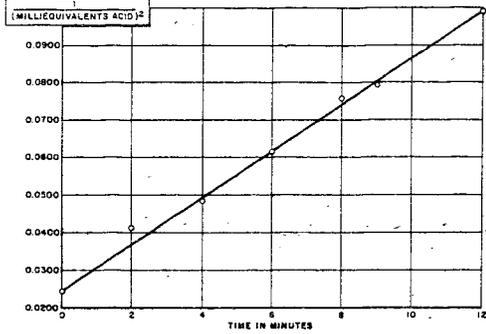


Figure 4

CURE RATE OF COAL ACIDS
PENTAERYTHRITOL RESIN AT 230°C.

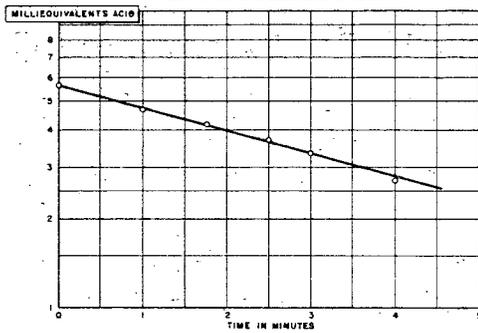


Figure 5

SAPONIFICATION RATES OF COAL ACID
RESINS IN N/10 NaOH

RATIO OF ALKALI TO RESIN = 1/1.4

