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Coal Acids - Raw Material for Foundry Resins

By
Wesley L. Archer, James B. Louch and Robert S. Montgomery

The Dow Chemical Company - Midland, Michigan

INTRODUCTION:

Aromatic polycarboxylic acids derived from the controlled oxidation of coal(1) have been used to prepare thermosetting resins of interest to the foundry industry. The monoethanolamine, diethanolamine, ethylenediamine, diethylenetriamine and pentaerythritol adducts of these coal acids were investigated as shell molding resin binders.

The current uses of a phenol-formaldehyde resin in the foundry industry illustrates some of the market potentials for the new coal acid resins. The largest market is found in shell molding where some 17 million pounds of phenol-formaldehyde resin was used in 1957. The increased use of the phenol-formaldehyde resin with cereal binders in steel cores is another market with good growth potential.

Sand briquettes bonded with the coal acid resins were tested for tensile strength and the resins of particular interest evaluated in shell molding. The coal acid - pentaerythritol preadvanced resin was outstanding in overall performance as a shell molding binder and thus will be the resin of prime interest in this paper.

Resin Preparation

The resin adducts of interest in this investigation were homogeneous solutions of the coal acids and reactant in water. The coal acid - pentaerythritol resin was partially advanced in water to give a still water soluble homogeneous solution. These water solutions afford an easy and economical method of applying the resin to the sand. In most cases, equivalent ratios of the reactants were used in the resin preparation and resin adduct concentrations of 60-70% gave solutions of workable viscosities. The resins as water solutions have an unlimited storage life.

Requirements of a Shell Molding Resin

The first requirement of a shell molding resin is that it must give a free flowing resin coated sand which on heating thermosets to firmly bond the sand grains together. The resultant shell mold must have sufficient heat resistance to withstand the shock of molten metal and hold close tolerances until the metal has set. At the proper time in the metal set cycle the shell must also burn out to give collapse of the shell and a clean casting. The temperature of collapse can be governed by the resin type and concentration, e.g. urea formaldehyde gives a low temperature collapse for magnesium and aluminum castings. Phenolic resins afford higher heat resistance and are commonly used for malleable iron and steel castings.

The potential resin binder must be effectively and easily dispersed in a sand mix by means of a Simpson or similar type muller. Dry blending of the sand and powdered resin has been popular in the past, but it is rapidly being replaced by a more effective liquid resin coating procedure. In this procedure a source of hot air may be used during the mulling operation to dry the resin coated sand until it is free flowing. Maintenance of this free flowing condition during storage is necessary for optimum pattern performance later.

It is important that the resin binder be cured and thermoset within a reasonable period of time. The approximate time and temperature limits are illustrated in the typical shell molding procedure given below.

(1) The dry resin coated sand is dropped onto a preheated (400-500°F.) metal pattern and allowed to remain for 15-35 seconds. This time period known as the coat or dwell time determines the thickness of the shell.

(2) At the end of the proper dwell time the entire pattern is inverted 180 degrees allowing all the excess and unbonded sand to fall back into the dump box. A dough like shell of resin bonded sand is left adhering to the metal pattern.

(3) The metal pattern and partially cured shell is then placed in an electric or gas furnace (800-1400°F.) where the cure is completed in 40-60 seconds.

(4) The thermoset shell mold is then ejected from the metal pattern by hydraulically operated ejection pins.

The fabrication performance and pouring behavior of the shell mold is greatly dependent on the shell having sufficient tensile strength at a reasonable resin concentration, e.g. 3.5-5% resin solids. Factors that affect the tensile strength of the resin bonded sand include the resin's actual composition, the efficiency of the coating operation, the degree of resin flow before thermoset and the temperature range necessary for this flow. All of these factors and the conditions necessary for the optimum tensile strength can be evaluated by preparing briquettes from the dried resin coated sands.

Preparation of the Coal Acid - Pentaerythritol Resin -(ET-400)

Most of the coal acids used in this work were prepared at the Dow Chemical Company. These coal acids were similar to those made by the Carnegie Institute of Technology (2) and had an equivalent weight of 80-85 and average functionality of approximately three.

The first partially esterified coal acid - pentaerythritol resins were prepared by stirring and refluxing the mixture for a period of 3-6 hours. The degree of advancement was determined by titration of the available carboxylic acid groups. The reaction of a 75% solids solution of 1 equivalent coal acids - 1 equivalent pentaerythritol during the first two hours of reflux is rapid. An equilibrium esterification of 38% was obtained after 8 hours. When 0.9 equivalent of pentaerythritol (75% solids solution) is used an equilibrium esterification of 32% is reached after 8 hours. The effect of solids concentration on the esterification rate is shown by the fact that a 90% solids solution of ET-400-85 (contains 0.85 equivalent pentaerythritol) gives 25% esterification at the end of the first twenty minutes of reflux.

The partially advanced resin is a viscous solution which does not exhibit any precipitation on standing if the advancement is greater than 12%. The resin solution at 60-65% calculated reacted solids gave a very workable viscosity.

Physical Properties of the Coal Acid - Pentaerythritol Resins -(ET-400)

Preparation of one quarter inch briquettes from the dried resin coated sand allowed a study of the physical properties of the coated sands as they were related to the resin composition and pretreatment. The sand coating operation was done in a "Kitchen Aid" mixer or in large batches in a Simpson Muller. A source of hot air directed onto the sand mix shortens the time required for the mulling operation. After screening the coated sand through a 42 mesh screen it was dropped into a quarter inch deep briquette mold preheated to 425°F. The coated sand was allowed to stand for 10-15 seconds and then the excess unbonded sand scraped off with a thin metal strip. Curing of the briquette at 650°F. for 2 minutes gave the finished test specimen. These were then tested on a motor driven Dietert Tensile Tester.

A. Optimum Pentaerythritol Concentration in ET-400

Tensile strength determinations have shown that the pentaerythritol concentration can be dropped to 0.9 equivalent pentaerythritol to 1.0 equivalent coal acids without reducing the resin's bonding strength. Use of a 1:1 ratio of hydroxyl to carboxylic acid groups would seem unnecessary since steric hinderance undoubtedly prevents the reaction of some of the carboxylic acid groups.

B. Physical Strength vs. Resin Concentration

A plot of the percent of reacted resin solids on a coarse Ottawa sand vs. the resultant tensile strengths is shown in Figure 1. The briquettes were bonded with an ET-400-9 resin with a preadvancement of 17.5% and cured for 2 minutes at 650°F. A tensile strength of 360 psi. is obtained at the 4% resin level commonly used in commercial shell molds. Naturally, the strength at a certain resin level will vary with the size distribution of the sand, the clay content of the sand, the resin composition and the coating techniques. Each of these factors will be discussed later.

C. Effect of Resin Preadvancement

The tensile strength of the ET-400 resin coated sand has been found to be a function of the resin preadvancement. The preadvancement necessary for optimum tensile strength appears to be in the range of 13-18%. Figure 2 shows the effects of preadvancement on the tensile strengths of two different resin coated sands. This particular data was obtained on small one and a half pound batches of sand coated in a "Kitchen Aid" mixer. The one tensile strength value in Figure 2 marked muller demonstrates that higher tensile strengths may be expected from the more effective coating obtained with a Simpson Muller.

The presence of clay and other nonsilica impurities in the Vasser bank sand could explain the differences in tensile strength of the Vasser bank AFS 100 sand as compared with the high silica content Wedron AFS 116 sand. The clay and silt impurities could indeed decrease the flow of the resin before the thermoset. Thus, flow of the resin coating on a sand grain to the surrounding sand grains and formation of a complete bond would be decreased.

The most important property controlled by resin advancement is the rate and temperature at which the resin flows. The improved flow behavior of the resin on coated sands with less preadvancement is directly reflected in the improved tensile strengths. The temperature at which the resin film on a sand grain will start to flow can be determined and is referred to as the stick point. A lower preadvancement of the ET-400 resin gives a lower stick point and a resultant higher tensile strength.

Preliminary observations have shown that the amount of moisture pickup by the resin coated sand is another factor controlled partially by the degree of resin advancement. Thus, adequate resin advancement is necessary so that the resin coated sand will remain in a free flowing condition before actual use. Sand coated in a Simpson Muller with a resin of at least 15% preadvancement will give a stable free flowing sand. This range of resin preadvancement may also be expected to give nearly optimum tensile strengths.

Shell Mold and Core Fabrication

The ET-400 resin with optimum sand binding properties was then examined in the actual fabrication of shell molds and cores. The small three prong cover plate type shell mold that was prepared on a small dump box machine is shown in Figure 3. Hollow shell cores have also been prepared on a commercial Shalco core blowing machine. Both pieces of equipment employ the same basic principles of investment, removal of excess unbonded sand and final cure as outlined earlier.

A. Sand Coating Procedure

The proper mulling procedure is second only to the resin in determining the final behavior of the coated sand in shell mold fabrication. The resin formulations for actual shell fabrication were applied to 20 pound batches of sand contained in a Simpson Muller.

A typical coating operation for the Simpson Muller is given below:

(1) Charge 9000 grams of sand and 550 grams of liquid ET-400-9 resin (4% reacted solids on sand) and 20 grams Acrawax (0.22%) to the muller.

(2) Mull for 1 minute.

(3) Hot air supply started and continued until coated sand went through the agglomeration stage.

(4) Mulling continued for an additional 15 minutes with hot air.

(5) Coated sand dumped and screened through a 40 mesh screen.

The Acrawax serves as a lubricant for the final resin coated sand and helps the sand retain its free flowing character. The hot air for the mulling operation was furnished by a small modified hair dryer with a maximum nozzle temperature of 500°F.

During the agglomeration stage it was found necessary to stop the muller several times and manually break up the plastic like sand mass. Coating of 720 pound batches of Nugent AFS 75 sand with ET-400 in a commercial size muller did not give this problem. The entire cycle from resin addition to coated sand discharge required 14 minutes in the commercial setup. Total time for the coating operation in the small Simpson Muller was 35 minutes.

B. Shell Mold Properties

A Nugent AFS 75, coarse Ottawa or Wedron AFS 116 sand coated with 4% of ET-400-9 resin gave good three prong cover plate shell molds at a pattern temperature of 450-500°F., investment time of 15 seconds and cure time of 40-60 seconds. A resin preadvancement of approximately 15% is preferred for maximum tensile strength and pattern performance at a low pattern temperature of 450°F. Moisture stability of the ET-400-9 coated sand appears to be good since no buildup of coated sand on the back side of the shell and/or peel back of a portion of the shell occurs. An excessive amount of moisture also tends to cause the agglomeration of the individual sand particles into units of several particles. These small agglomerates give poor packing of the sand particles at the pattern surface and the resulting poor surface hardness and strength.

The differences in tensile strengths of a high silica sand and bank sand shell mold is again illustrated by the following values. The tensile strength of the 4% ET-400-9 (advanced 16%) coated Nugent sand averaged 315 psi. as compared to the value of 795 psi. for the resin on Wedron sand. Hardness as measured by a Dietert Hardness Tester was 80 for the Nugent shells and 90 for the Wedron sand shells.

Recent work has shown that the addition of a nonionic surfactant, e.g. 0.25% Triton X-100, to the resin coated Nugent or Vasser sand will give a 25% strength increase. Replacement of 30% of the pentaerythritol in the ET-400 resin with a glycol or ethylene oxide adduct will also give a 25-40% increase in the resin strength. Thus the tensile strength of a modified 4% ET-400-9 coated Nugent sand can be expected to average 400-450 psi.

A field test of the ET-400-9 resin as a shell molding binder has been attempted at a malleable iron foundry. The resin used in this test was one of the earlier ET-400-9 formulations preadvanced to 28.5%. The performance of the resin in the coating of the Nugent sand in 720 pound batches was good. Shell molds of 20 x 30 inches in size were fabricated at a pattern temperature of 500°F., investment time of 34 seconds, and cure time of 50-60 seconds. Figure 4 shows one of the 20 x 30 inch shell molds being ejected from the pattern after cure. Approximately 25 castings weighing 11 pounds a piece were successfully cast without any major metal breakouts. The major point for improvement appeared to be the need for increased tensile strength. Tensile bars prepared from this coated sand gave an average tensile strength of 170 psi. The ability of the newest ET-400 formulation to give some 400 psi. strength on Nugent sand may give the needed additional strength for a completely successful commercial test.

C. Shell Core Properties

Acceptable commercial hollow shell cores (23 inches in length and 2-5 inches in width) have been fabricated on a Shalco core blowing machine using a 3.5% ET-400-9 coated Wedron sand. The resin had been advanced to 28.5% esterification. Shell cores with excellent hardness (90 on Dietert Tester), detail and strength were prepared at 600°F. with an investment time of 5-15 seconds and cure time of 1.5-2.0 minutes. These conditions correspond to cure conditions used with a commercial phenol-formaldehyde resin coated high silica sand.

Core Binders

The foundry industry's interest in improved core binders has encouraged the use of the urea formaldehyde and phenolic formaldehyde resins. Principle use of the phenolic resin in solid foundry cores has been limited mostly to steel cores. The need for a more heat resistant binder for steel cores has limited the resin to a phenolic type. The cheaper urea formaldehyde type resin finds wide use in the nonferrous and ferrous type foundries. Both resins are used in conjunction with various cereal flours and core oil binders.

Preliminary data indicates that several of the coal acid type resins may find utility in foundry cores. Specifically, cores with tensile strengths of 570 psi. have been prepared from an Ottawa AFS 60 sand bonded with 1.0% ET-400-9, 1.0% Mogul B211 flour and 5% water. Core mixes of this type have been successfully core blown with commercial machines. The tensile data of other coal acid resins given in the preceding paper also suggests the possible use of these in the core binder application.

Preparation of briquettes from a moist resin coated sand and allowing the briquettes to stand at room temperature leads to the development of considerable green strength. This green strength is the result of the air drying of the resin film to give a "dry" water plasticized resin film surrounding and bonding each sand particle. The diethanolamine resin adduct for example, yields an optimum strength of 325 psi. at a 6% resin concentration while 6% of the diethylenetriamine adduct gives a green strength of 240 psi. after only 20 hours at room temperature. This green strength property could also be of interest in sand core fabrication.

CONCLUSIONS:

Increasing foundry interest in new synthetic thermosetting sand binders has opened markets for resin binders that have new and improved physical properties. A new type of sand binder for this purpose may be derived from the oxidation products of bituminous coal. Specifically, thermosetting resins may be prepared from these coal acids and an alkanolamine, polyhydroxyl or polyamine reactant.

The coal acid - pentaerythritol resin (ET-400-9) preadvanced to 13-18% esterification is of particular interest in shell molding work. A 13-18% preadvancement will produce a free flowing sand with optimum tensile strength. Experimental shell molds have been prepared with this ET-400-9 resin at a pattern temperature of 450-500°F., investment time of 15 seconds and cure time of 40-60 seconds. Both high silica content sands and bank sands have been used in the shell mold fabrication. At a 4% resin concentration 315 psi. of tensile strength can be expected with a medium fine, unwashed bank sand. The addition of a surfactant to the resin increases the strength of the resin bonded bank sand to 400 psi. Use of a fine, washed high silica content sand increases the tensile strength to 795 psi.

One attempt to use ET-400-9 as a commercial shell molding binder indicated that a somewhat greater tensile strength is necessary. A new formulation with only 15% advancement may afford the needed strength improvement. Tensile strengths of the original resin bonded sand were 170 psi. as compared to the later tensile strengths of 400 psi. (contains 0.25% surfactant). Commercial shell cores have also been fabricated with ET-400-9.

REFERENCES:

1. Montgomery, R. S., Holly, E. D. and Gohlke, R. S., Fuel, Lond., 35 (1956) 60
   Montgomery, R. S., Holly, E. D., ibid. 36 (1957) 63

2. Franke, N. W., Kiebler, M. W., Ruof, C. H., Sovich, T. R., and Howard, H. C., Ind. Eng. Chem., 44, 2784 - 2792 (1952).

Figure 1

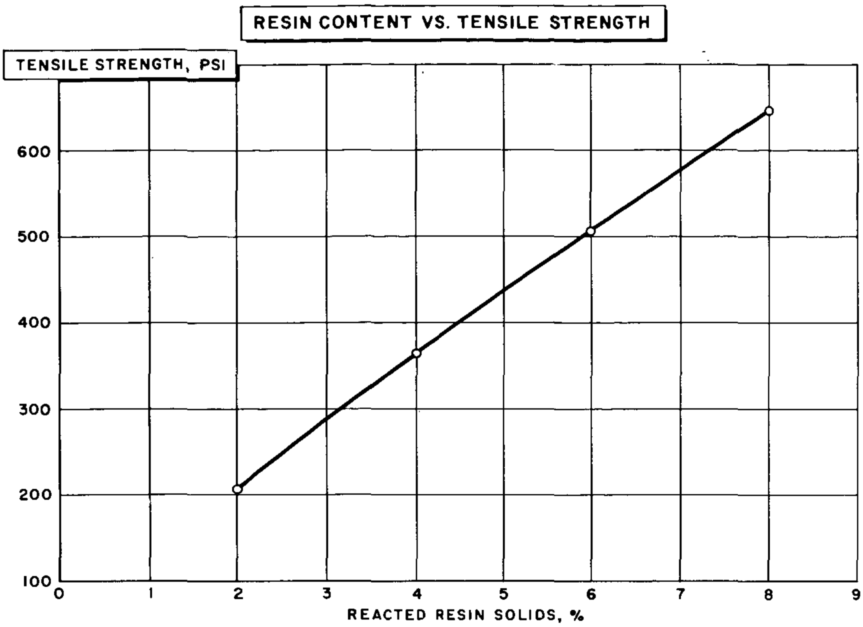

Figure 2

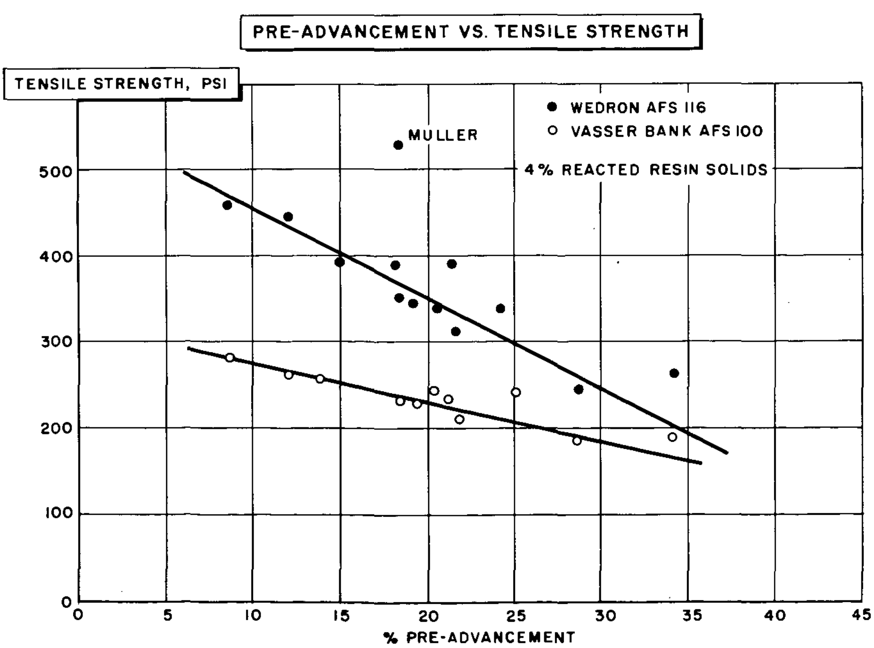

Figure 3

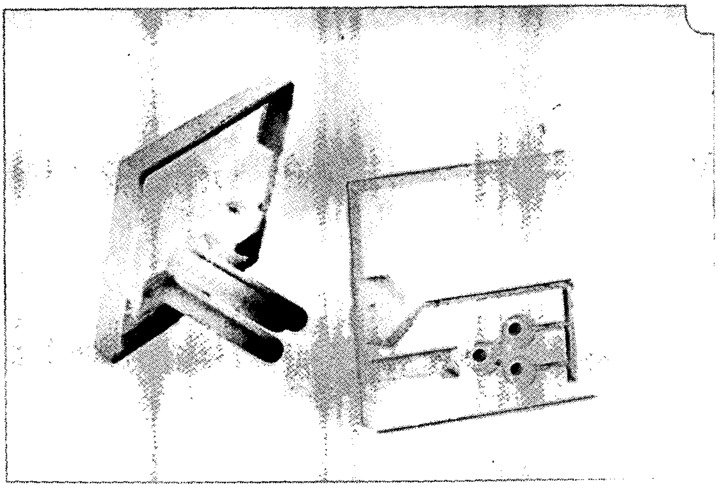

Figure 4