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Finding Commercial Uses for the Coal Acids

By

R. S. Montgomery

The Dow Chemical Company, Midland, Michigan

When we began our work on the mixed acids obtained by the caustic-oxygen oxidation of bituminous coal, our first concern was to find commercial applications for them. Just as with any other research chemical, the important question was, "What are they good for?". Basically, the coal acids are a complex mixture of polyfunctional aromatic acids with benzene, naphthalene, and biphenyl as the chief nuclei. (1) The average molecular weight is about 270 and the average equivalent weight about 81. Therefore, the average functionality is about 3.3. They are made by oxidizing a suspension of bituminous coal in aqueous sodium hydroxide by means of gaseous oxygen at a temperature of about 290°C. and a total pressure of about 1800 p.s.i.g. (2) In this paper, I plan to discuss our general plan of attack on the problem of finding out "What are they good for?".

INITIAL WORK

The most obvious line of attack and the one generally used at the outset in problems of this nature is to try to use the new chemical in applications where similar materials are now being used. A model compound of similar structure is selected and then one systematically attempts to substitute the new compound for this compound in all the areas where it is being used. The only polyfunctional aromatic acid of much commercial importance is phthalic acid and so it is natural to select this acid as our "model compound". This leads us to an investigation of the possible use of the coal acids in plasticizers, plating baths, synthetic lubricants, alkyd resins, and the like. We investigated these uses as did other investigators a good deal prior to us. (3)(4)(5) In general, however, this approach was not very profitable mainly because the coal acids are really not very similar to phthalic acid. In the first place they are a complex mixture rather than a single chemical species. In addition, they are water-soluble, rather dark colored, and have higher functionalities and molecular weights than does phthalic acid. Because of this, the coal acids appear to be inferior to phthalic acid in all the applications where phthalic acid is commercially used.

SEPARATION

The next logical line of attack on this problem is to attempt to separate the mixture into its components. If this is not feasible, perhaps the mixture could be fractionated into simpler mixtures or perhaps at least the dark colored components could be removed. Previous investigators had attempted to separate the mixture by distillation of the esters and by solvent fractionation. (6) We investigated these methods (7)(8) and also investigated a fractionation based on differences of acid strengths (8) and even partition chromatography. (9) None of these methods was suitable for the commercial separation of the components and only the fractionation based on the different acid strengths appeared to be of any commercial importance. With this method, a reasonable fractionation can be obtained as can be seen from Figure 1 but the fractions are still dark-colored and are still complex mixtures. The dark-colored components could not be removed although some of the fractions obtained by the distillation of the esters, chromatography, and solvent fractionation were lighter in color than others. Treatment of the mixture with hydrogen, hydrogen peroxide (10), carbon, and sodium hypochlorite were all quite ineffective although the hypochlorite treatment did give some improvement.

THERMOSETTING RESINS

After the only very limited success of these two lines of attack, some new point of view was required so we then began to look at the coal acids as a basically new and different chemical and began to try to exploit its unique properties. The properties that seemed the most important were the high functionality, aromatic character, and perhaps the water solubility. Although many applications were investigated from this point of view, I will discuss only the ones that appeared to be of the most interest.

The high functionality of the coal acids suggested that they might be useful in a highly crosslinked, thermosetting resin. Their aromatic character led us to believe that they could also contribute good heat stability and good resistance to oxygen attack. Therefore, we felt that we could, perhaps, make good, relatively heat-resistant binder resins from them and we began to look for applications requiring resins of this kind. In addition, the fact that the acids were water-soluble allowed the uncured mixture or the partially cured resin to be applied directly from a water solution. This lead us to investigate these coal acid resins as foundry binders, plywood and hardboard binders, glass fiber binders, etc. Two of the following papers will be concerned with these applications so I will not go into them any further.

WARP SIZE

Another unique property of the coal acids is their ability to form films. An aqueous solution will dry to a rather tough, pale-yellow film. This behavior is unusual for a material of molecular weight on the order of 270. The viscosity behavior of a concentrated aqueous solution, however, provides an insight into the reason for this property. From Figure 2 it can be seen that the coal acids in dilute solution behave as individual monomeric units of about 270 molecular weight but as the solution becomes more concentrated, the viscosity increases more rapidly than can be accounted for by just the increased concentration. The molecular weight increases as the concentration increases until at very high concentrations we have, in effect, a high polymer. This is probably due to the formation of hydrogen bonds as the monomeric units are brought closer and closer to each other when the solution becomes more concentrated and can be considered as actually a kind of reversible polymerization. Perhaps then, the coal acids could be used in applications where water-soluble polymers are used. We investigated several of these applications and the most promising appeared to be textile warp sizing. This specific application will be discussed in a following paper so I will not say much about it but I would like to emphasize the fact that this use is based on the unique physical behavior of the coal acids and would not be expected on a basis of the physical properties of other known aromatic acids.

SLURRY THINNING

Another application based on the unusual water solubility of the coal acids is that of slurry thinning. It was already known that the sodium salts of the coal acids were useful as slurry thinners for weighted drilling muds. (11) Normally only the salts of large molecular weight organic acids have the required solubility for this application but in this case the acids themselves can be used. The coal acids themselves have shown a much wider applicability than did their sodium salts. For instance, the coal acids are useful for thinning ordinary drilling mud as well as weighted drilling mud. Figure 3 shows the viscosity of bentonite drilling mud as a function of the amounts of both the coal acids and their sodium salts. This again is an example of a use based on the unique properties of the coal acids.

CONCLUSIONS

In conclusion, I would like to re-emphasize the fact that very often, as in this case, the more conventional ways of investigating the utility of a new material may be unproductive but a fresh point of view may provide us with an important new use based on one or more unique properties of the material. In the case of the coal acids, their use in thermosetting resins, as water-soluble film formers, and as slurry thinners are all based on unique properties and would not be predicted on a basis of the properties of other aromatic acids.

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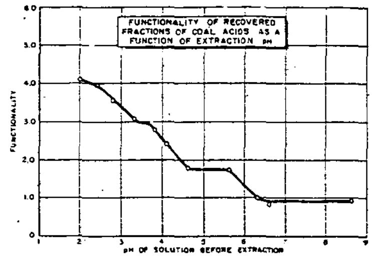
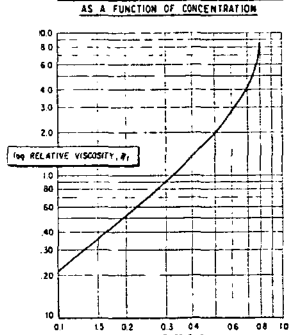


VISCOSITIES OF AQEOUS COAL ACID SOLUTIONS AS A FUNCTION OF CONCENTRATION



VISCOSITY OF A 7% BENTONITE SLURRY AS A FUNCTION OF AMOUNT OF ADDITIVE