COAL CHEMICALS FROM COAL OXIDATION PRODUCTS

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Coal can be oxidized in various ways to yield mixtures of organic acids. The product obtained, of course, depends to some extent on the specific process. The process that The Dow Chemical Company has felt to be the most promising involves the oxidation of a suspension of bituminous coal in aqueous sodium hydroxide by means of gaseous oxygen under high pressure. This process requires about three pounds of sodium hydroxide for every pound of coal oxidized. The Dow Chemical Company as you know is a large producer of chlorine and sodium hydroxide. Since we have large internal requirements for chlorine without the equivalent requirements for the sodium hydroxide produced as a co-product, this process would seem ideal for us. The process that we used is basically the process developed by The Coal Research Laboratory of The Carnegie Institute of Technology.[1] We did, however, refine this process somewhat by using a more sophisticated, multiple-chamber, stirred reactor so that the process could be carried out continuously. The Coal Research Laboratory had used a simple stirred autoclave, but of course recognized that this reactor would probably be modified to allow continuous operation in an actual commercial process.

The oxidation products obtained by this process are sodium carbonate, a relatively small amount of the base-soluble, water-insoluble, humic acids, and the most important product, a light-yellow colored, water-soluble mixture of aromatic acids. The average molecular and equivalent weights of these so-called "coal acids" are about 270 and 82 respectively, resulting in an average carboxylic acid functionality of 3.3. The main components of this mixture are the various benzene, naphthalene, and biphenyl polycarboxylic acids; 1,2,4 benzenetricarboxylic acid, which constitutes about 21% of the mixture, is the most important single component.[2,3,4,5] The separation or even fractionation of this mixture is difficult and expensive[6] and so any commercial use for it will probably, at least initially, be a use for the mixture as a whole without any extensive separation.

There are many potential uses for the coal acids, and some of them appear to have a great deal of promise. This product is quite unique in that these acids are almost completely aromatic but have sufficient polyfunctionality so that they are readily soluble in water, and instead of crystallizing, form an amorphous film on the removal of the water. This great difference between the coal acids and currently available aromatic acids is both a strength and a weakness. It is a strength because there is the possibility that very large amounts could be required for applications where virtually no substitutes could be found. It is a weakness in that there is no ready-made market for a material of this kind, and it is difficult to assess accurately the volume that could be sold and the value that it would have to the consumer.

The acids themselves and their salts have been suggested as substitutes for other water-soluble acids in various applications,[1] and in addition have been used as corrosion inhibitors[7] and as a set retarder for gypsum[8]. One application for these acids that is certainly not obvious is their use as a warp size for synthetic fibers. The coal acids were found to be an excellent warp size for nylon, polyester fibers, and cellulosics.[9,10,11] The reason for this is that these polyfunctional acids interact more and more strongly by hydrogen bonding as their aqueous solution becomes more and more concentrated until finally they form, to all intents and purposes, a "high polymer" at very low water contents. These crosslinking hydrogen bonds are cleaved by water and so this "high polymer" is still perfectly soluble in water. Although the coal acids make an excellent warp size, they do have a very real disadvantage. Textile mills are naturally reluctant to use a colored size on an expensive fiber even if they are assured that it can be entirely removed after weaving.

Perhaps the most obvious derivatives of an organic acid to be investigated are the esters, and it was found that the various esters of the coal acids could be used as plasticizers,[1] synthetic lubricants,[12] hydraulic fluids,[13] and corrosion inhibitors.[14] Here again their color mitigated against their use in plasticizers and they did not possess any property, including potential price, that would make them extremely interesting for these applications. If they were available there would doubtless be some sold for these purposes, but a production plant would not be constructed on the strength of these applications.

The most promising application for the coal acids is their use in thermosetting resins. They can be reacted with an alkanolamine,[15] alkylene oxide, polyhydroxyl compound[16], or polyamine[17] to give a wide spectrum of resins with varying properties. The polyamide, polyester, or combination of functional groups possible in these resins are illustrated in the following examples:

$$R(COOH)_3 + HN(CH_2CH_2OH)_2 \longrightarrow R(COOCH_2-)_2(CONCH_2-) \qquad (1)$$

$$R(COOH)_2 + HOCH_2CH_2OH \longrightarrow R(COOCH_2^-)_2 \qquad (2)$$

$$R(COOH)_2 + H_2N(CH_2)_nNH_2 \longrightarrow R(CONCH_2^-)_2 \qquad (3)$$

$$1\ \text{eq.}\ R(COOH) + 1\ \text{mole}\ HN(CH_2CH_2OH)_2 \longrightarrow R\left[CON(CH_2CH_2OH)_2\right] \qquad (4)$$

$$R(COOH)_2 + \underbrace{CH_2CH_2O} \longrightarrow R(COOH)(COOCH_2CH_2OH) \qquad (5)$$

It is advantageous to prepare a partially cured but still water-soluble resin. Heating equivalent amounts of the coal acids and monoethanolamine at 170°C. for 3 hours gave 85% esterification, but very little amide formation. Other partially cured but water-soluble resins can be prepared by heating the coal acids with pentaerythritol, or ethylene, propylene, or butylene oxides. These partially cured resins are in the form of viscous aqueous solutions. They can be stored indefinitely in this form without any danger of further polymerization. This partially cured material will completely cure to a strong, insoluble, crosslinked structure when it is heated at elevated temperatures (over 200°C). In addition, these partially cured coal acid resins are compatible with the water-soluble phenol-formaldehyde prepolymers, and are incorporated in the phenol-formaldehyde polymer structure. The physical properties of the cured coal acid resins compare favorably with those of other thermosetting resins, and in addition at a suitably large volume their cost should be less than the other thermosets.

These coal acid resins could be used for many purposes such as plywood, hardboard, and chipboard binders[18], binders for fiberglass, and shell molding and foundry core resins[19]. There has been a great deal of work done especially in the field of foundry resins, and these resins have shown considerable utility. The extremely long pot life is a definite advantage for many uses, but the attendant relatively high curing temperature is a disadvantage when the resin is used to bind thermally sensitive materials. In any case the coal acid resins are very promising and appear to represent the best possibility for a large-scale use for the coal acids.

The final portion of my talk will be concerned with the question of the economics of producing a product such as this and why The Dow Chemical Company has not begun commercial production. Basically, the coal acids are a low-priced product. If they are to be commercially successful they must compete pricewise with the products which will do a similar job in a particular application, and in general these are high-volume, relatively low-priced chemicals. In addition to being a low-priced product, the coal acids also require a large capital expenditure for production facilities. For a product of this kind requiring a large capital expenditure, there is a characteristic volume-cost curve. At high production rates the cost is low, but where a high production rate is not justified, the product is very expensive to produce. Therefore a company embarking on the commercial production of a product such as this must take a calculated risk and construct a large production plant and price the product low in the hope of developing a large market for it which will justify this large plant and low price. If the market does not develop as hoped, a great deal of money could be lost. Therefore, what is needed to stimulate interest in the commercial production of coal chemicals from coal oxidation products is a single large-scale use which seems certain enough to justify the construction of a large production plant. At the present time the coal acid resins appear to represent the best possibility of obtaining this large-scale use.

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