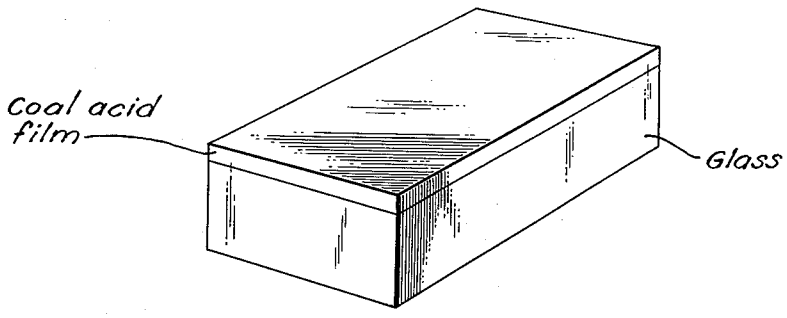
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METHOD OF COATING A SUBSTRATE WITH COAL ACIDS AND ARTICLE PRODUCED THEREBY

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METHOD OF COATING A SUBSTRATE WITH COAL ACIDS AND ARTICLE PRODUCED THEREBY

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This invention relates to protective coated articles or substrates and to their method of manufacture. More particularly, it relates to articles or substrates which have been coated with a coal acids-base water-soluble protective coating which affords scratch resistance, fire resistance, and non-polar organic solvent resistance properties to various articles of manufacture, which coatings can readily be removed when desired.

Many temporary protective coatings are known. The majority of those presently in use lack one or more desirable physical properties, present difficulties in their removal, or are relatively expensive.

It has now been discovered that coal acids can be deposited as films upon various substrates to provide relatively inexpensive protection against marring, and affording non-polar organic solvent resistance and fire resistance under conditions where water-solubility is not material. Because of their water-solubility, such films of coal acids are readily removable when desired by washing with water.

The coal acids utilized in this invention are advantageously applied as aqueous solutions. It is desirable that the final film contain between 0.5 and 10 percent by weight of water as plasticizer to improve flexibility. The water content of coal acids films is readily regulated by drying at relative humidities ranging between about 20 and 75 percent.

The most generally useful coal acids solutions contain about 30 to 85 percent by weight of coal acids, solution basis. They can be applied by brushing, spraying, dipping or equivalent means. Solutions containing between 30 and 70 percent coal acids are used for non-porous surfaces or where penetration is desired, while solutions containing between 70 and 85 percent coal acids are used where very porous surfaces are being coated or where a relatively thick film is desired. Room temperature drying is generally preferable.

Many types of substrates can be coated to deposit a coal acids film, for example, paper, wood, glass, metal, plastics, and the like.

It is sometimes desirable to include a small amount of a non-ionic wetting agent, for example, 0.2 to 5 percent by weight of coating composition, to facilitate levelling out.

The coal acids that are useful in the compositions of this invention are identical with or similar to those which are obtained by the oxidation with gaseous oxygen or air of an aqueous alkaline slurry of a finely divided carbonaceous material selected from the group consisting of coal or coke that has been obtained by the carbonization of coal at temperatures below about 700° C. Coal acids that have been obtained by the nitric acid oxidation of suitable carbonaceous materials are also satisfactory. Such coal varieties as anthracite, bituminous, sub-bituminous and lignite or other low grade coals are suitable for the production of coal acids. Satisfactory cokes are those produced according to conventional techniques from coal at a temperature below about 700° F. The utilization of higher coking temperatures frequently causes the cokes that are obtained to be graphitic and

rendered unsuitable for conversion to coal acids in satisfactory yields.

The preparation of coal acids from coal may, by way of illustration, involve mixing a ground bituminous coal with a caustic alkali, such as sodium hydroxide, and water, using an excess of the caustic with respect to the amount that is contemplated as being required for neutralizing the coal acids formed. Generally, an apparatus is employed that is constructed from a corrosion-resisting material of construction and that is adapted for operation under pressure. The apparatus is also equipped with an efficient mixing or agitating mechanism and with suitable heat-exchanging means. The weight ratio of the charged ingredients may, for example, be in the proportion of about 3 parts by weight of the coal to 9 parts by weight of the caustic alkali to 125 parts by weight of water. Oxygen is bubbled through the agitated charged ingredients while they are maintained at a temperature between about 200 and 300° C. and under a pressure of from about 500 to 1200 pounds per square inch. The exothermic reaction is continued until substantially all of the carbonaceous ingredients of the coal have gone into solution. This usually requires a period of time between about 2 and 3 hours. In the oxidation reaction that occurs, about half of the carbon in the coal is converted to organic acid compounds while the remainder is oxidized to carbon dioxide. Upon termination of the reaction and cooling of the reaction mass, the coal ash is filtered out of the alkaline solution that is obtained.

The coal acids may then be isolated by acidifying the solution with a mineral acid, e.g., sulfuric acid and, after filtration, recovering the free, water-soluble coal acids by extraction with a suitable solvent, such as methyl ethyl ketone, which does not dissolve in water in the presence of such salts as sodium sulfate which are obtained in the acidified free coal acid solution. Known evaporation and drying techniques are employed for subsequently isolating the free coal acids. The coal acids may thus be prepared as solid materials that are often pulverized for subsequent handling in a powder form.

The free coal acids product is a hygroscopic, usually yellowish, essentially water soluble material, believed to be comprised substantially of various aromatic polycarboxylic acids. The average molecular weight of the coal acids that are ordinarily obtained is usually in the neighborhood of 250. Their average equivalent weight is generally about 80. They ordinarily appear to have an average of 2.5 to 5 carboxylic groups per molecule with an apparent average of about 3 to 4 being common. They evidently contain considerable quantities of tri- and tetracarboxylic benzene acids as well as aromatic acids having more complex nuclei. Frequently, for example, the greatly preponderant proportion of aromatic nuclei obtained in coal acids prepared in the described fashion have been found to consist of methylnaphthalene, benzene, biphenyl, naphthalene, phenanthrene, alkylbenzene, benzophenone and toluene nuclei.

The single figure drawing illustrates one of the embodiments of the invention.

The following examples represent specific embodiments of this invention.

EXAMPLE 1

A 50 percent by weight aqueous solution of coal acids was brushed on the surface of a glass plate. Upon evaporation of water at room temperature at a relative humidity of about 50 percent the dried film was clear, strongly adherent and resistant to removal by petroleum ether, toluene and methylene chloride. The blue flame from a Bunsen burner caused the film to char but not to flame. Combustion did not continue after removal of the Bun-

sen burner flame. A perspective drawing of a glass plate coated with such a film of coal acids is shown in the figure.

EXAMPLE 2

A 75 percent by weight aqueous solution of coal acids was applied to 40 pound unbleached kraft paper by means of a conventional number 20 Meyer wire rod and dried at room temperature. The dried film had a thickness of 0.003 in. Four-inch square test specimens of coated paper resisted the passage of turpentine for more than 1800 seconds, as determined by the method of ASTM D722–45, modified in that only 4 test specimens were run and in that two 1 in. square magnesium blocks weighing 55 grams total were placed over the turpentine-wetted sand to insure better contact with the paper. The same paper was coated with a 0.002 in. film of 60 percent styrene-40 percent butadiene copolymer latex and was subjected to the same test. It was penetrated in 600 seconds by the turpentine.

EXAMPLE 3

Comparative fiberboard packs were coated to give approximately the same film thickness with an aqueous 75 percent by weight coal acids solution and with 5 percent by weight 15 centipoise methylcellulose solution. One set of comparative fiberboard packs was filled with standard petroleum base grease. The other set was filled with S.A.E. 50 oil. The time necessary for the grease and the oil to spot the outside of the fiberboard packs was noted with the following results:

A. *Grease screening tests*

Coating:	Spotting time, hours
None	40
Methylcellulose	475
Coal acids	620

B. *Oil screening tests*

Coating:	Spotting time, hours
None	3
Methylcellulose	21
Coal acids	80

EXAMPLE 4

A 50 percent solution of coal acids in water was brushed on the following substrates:

1 in. x 3 in. x ⅛ in. mild steel sheet
1 in. x 3 in. x ⅛ in. polystyrene sheet
½ in. x 5 in. x ⅛ in. plastic sheet (copolymer of 80 percent styrene and 20 percent methacrylic acid)
⅛ in. x ½ in. x 2 in. plastic sheet (copolymer of 60 percent styrene and 40 percent vinyl cyanide)

The solutions on all four substrates were dried at 50 percent relative humidity to give continuous protective films 2 to 4 mils thick.

EXAMPLE 5

A 30 percent solution of coal acids in water was brushed on a series of three glass plates. The three plates were placed in series in three humidity chambers maintained at 20 percent, 51 percent, and 76 percent relative humidity, respectively. The solutions on all three plates dried to give continuous protective films 2 to 3 mils thick. The film dried at 76 percent relative humidity was somewhat sticky, while the other films were tack free. A 75 percent solution of coal acids gave substantially the same results as were obtained with the 30 percent solution.

EXAMPLE 6

An 85 percent solution of coal acids was applied to a series of three pieces of kraft paper with a No. 20 Meyer wire rod. The coated papers were placed in saries in humidity chambers maintained at relative humidities of 20 percent, 51 percent, and 76 percent, respectively. The solutions on all three papers dried to give continuous protective films 2 mils thick. However, the film dried at 76 percent relative humidity was somewhat sticky, whereas the other films were tack free.

What is claimed is:

1. A process for making a coated substrate having a water removable protective film which comprises depositing upon a substrate a continuous film of coal acids, said coal acids being the water-soluble, mixed aromatic carboxylic acids that are the products of the oxidation of carbonaceous materials, which acids typically have an average molecular weight of about 250, an average equivalent weight of about 80 and contain an average of from about 2.5 to 5 carboxylic groups per aromatic nucleus in their molecules.

2. The process of claim 1 wherein the substrate is coated with an aqueous solution of coal acids containing between 30 and 85 weight percent of coal acids, said coal acids being the water-soluble, mixed aromatic carboxylic acids that are the products of the oxidation of carbonaceous materials, which acids typically have an average molecular weight of about 250, an average equivalent weight of about 80 and contain an average of from about 2.5 to 5 carboxylic groups per aromatic nucleus in their molecules.

3. A substrate having a continuous water-plastified film of coal acids, said coal acids being the water-soluble, mixed aromatic carboxylic acids that are the products of the oxidation of carbonaceous materials, which acids typically have an average molecular weight of about 250, an average equivalent weight of about 80 and contain an average of from about 2.5 to 5 carboxylic groups per aromatic nucleus in their molecules.

4. Glass having a continuous water-plastified film of coal acids, said coal acids being the water-soluble, mixed aromatic carboxylic acids that are the products of the oxidation of carbonaceous materials, which acids typically have an average molecular weight of about 250, an average equivalent weight of about 80 and contain an average of from about 2.5 to 5 carboxylic groups per aromatic nucleus in their molecules.

5. Paper having a continuous water-plastified film of coal acids, said coal acids being the water-soluble, mixed aromatic carboxylic acids that are the products of the oxidation of carbonaceous materials, which acids typically have an average molecular weight of about 250, an average equivalent weight of about 80 and contain an average of from about 2.5 to 5 carboxylic groups per aromatic nucleus in their molecules.

6. Fiberboard having a continuous water-plastified film of coal acids, said coal acids being the water-soluble, mixed aromatic carboxylic acids that are the products of the oxidation of carbonaceous materials, which acids typically have an average molecular weight of about 250, an average equivalent weight of about 80 and contain an average of from about 2.5 to 5 carboxylic groups per aromatic nucleus in their molecules.

7. Polymeric styrene having a continuous water-plastified film of coal acids, said coal acids being the water-soluble, mixed aromatic carboxylic acids that are the products of the oxidation of carbonaceous materials, which acids typically have an average molecular weight of about 250, an average equivalent weight of about 80 and contain an average of from about 2.5 to 5 carboxylic groups per aromatic nucleus in their molecules.

8. Mild steel having a continuous water-plastified film of coal acids, said coal acids being the water-soluble, mixed aromatic carboxylic acids that are the products of the oxidation of carbonaceous materials, which acids typically have an average molecular weight of about 250, an average equivalent weight of about 80 and contain an

average of from about 2.5 to 5 carboxylic groups per aromatic nucleus in their molecules.

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