Jan. 26, 1965 G. C. HUETT ETAL 3,167,651

THERMOGRAPHIC REPRODUCTION PAPER AND METHOD OF MAKING AND USING

Filed May 15, 1962

FIG. 1

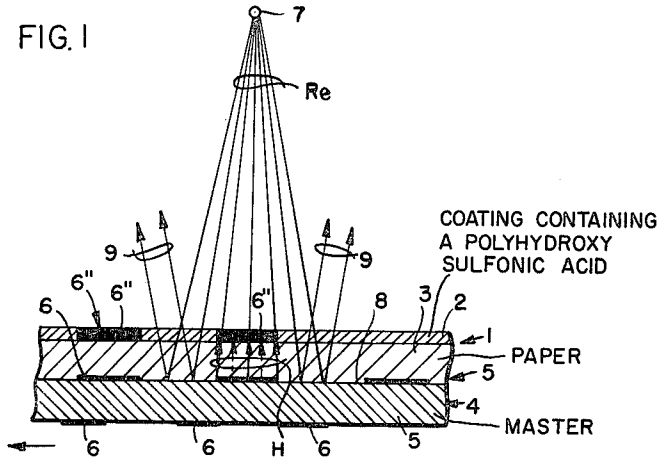
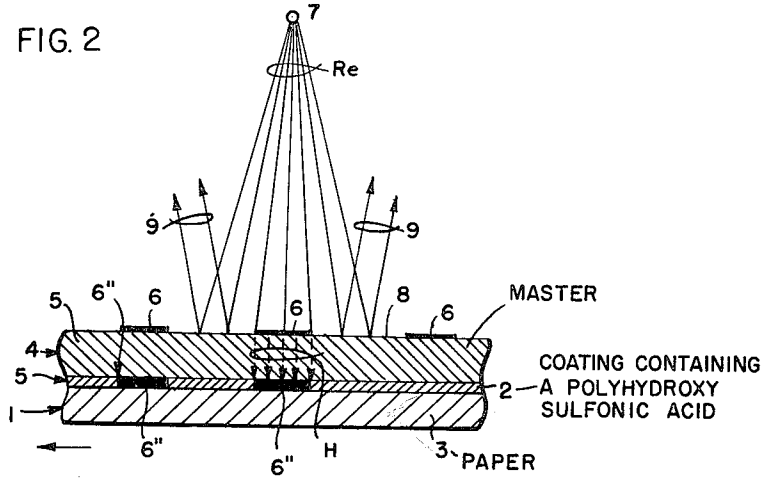


FIG. 2



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THERMOGRAPHIC REPRODUCTION PAPER AND METHOD OF MAKING AND USING

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The subject invention relates to the production of thermographic paper. More particularly, the present invention is directed to improved copying materials which are capable of producing a facsimile copy by means of radiant energy.

In the past several years, various types of copy paper have been developed which produce a facsimile copy when exposed to radiant energy such as infrared light beneath graphic subject matter set forth on an original. A typical thermographic process is described in the patent to Miller, U.S. 2,740,896. As is disclosed in this patent, carbon inks and certain other marking means absorb radiant energy from infrared bulbs creating heat. This energy is transferred to a sensitized sheet of copy paper in contact with the original causing the formation of duplicate characters.

A wide variety of materials have been used as color producing bodies in coating the copy paper. In heat developable diazotype reproduction systems, for example, the copy paper is coated with a diazo compound, a coupler, and a compound which produces an alkaline reaction when heated. In other systems such materials as nickel acetate, silver nitrate, sodium behenate, ferric stearate, etc., have been used as components of the color producing coating.

It has been found that compositions of the above type often have disadvantages, especially where the copy paper is to be used on a commercial basis. Such materials, for example, often tend to be unstable both prior to development and subsequent to the formation of the facsimile, which facsimiles cannot be used as intermediates for producing other copies. Additionally, many of the known coating compositions are relatively expensive and are difficult to handle on a commercial scale.

A novel thermographic process is described in our copending application Serial Number 185,347 which was filed on April 5, 1962, the disclosure of which is incorporated herein by reference. In this application a process is disclosed in which a suitable base is coated with a composition containing an organic acid and an aromatic polyhydroxy or polyamine compound. In certain embodiments of the process an aldehyde, a ketone, or an aldehyde forming compound is included in the composition. Under the influence of heat and a catalyst a reaction takes place between the components of the composition forming color bodies which duplicate the characters of an original.

A preceding and copending application Serial No. 181,091 filed on March 20, 1962, which is referred to in the above described copending application, covers a thermographic process in which either the cellulose in paper or carbohydrates coated on a suitable base are treated so as to produce a color image by means of radiant energy transferred from the characters of an original to the copy sheet. If the cellulose of the paper is to be transformed into a color-forming body the paper is treated with an aqueous solution containing particular amounts of particular acids. In a second embodiment the paper is coated with a solution of a carbohydrate such as lactose, glucose, mannose, etc., along with particular amounts of particular acids, and preferably along with certain stabilizing agents.

It is an object of the present invention to provide an

improvement in the above described thermographic processes.

Another object of the invention is to provide a new class of heat reactive copy papers which can be used to make reproductions from originals printed on one or both sides.

Another object of the invention is to provide thermographic reproduction paper which can produce images of originals having black characters as well as characters of certain other colors.

Still another object of the invention is to provide copy paper which will produce accurate and clear facsimiles.

Yet another object is to provide copy material which can be used to produce read out copies or intermediates regardless of whether the copy material is coated on one or both sides.

Another object is to provide copy material which can be used to reproduce originals by a reflex technique.

Still another object is to provide copy paper which can be used to produce originals by a heat transmission technique.

A still further object of the invention is to provide copy paper which can be used to produce facsimiles having well defined characters without causing the blurring of surrounding background areas.

Other objects will become apparent to those skilled in the art from the following detailed description of the invention.

In general, the present invention comprises the discovery that improved thermographic reproduction material is obtained by coating a suitable base with a solution containing as a solute an aromatic, polyhydroxy sulfonic acid. A typical sulfonic acid of the type used in the process is pyrogallol sulfonic acid. After the base has been coated with the sensitizing solution the base is placed in contact with an original which can be printed on one or both sides. The resultant sandwich is subjected to radiant energy such as visible light in the orange and red spectral zones or invisible infrared radiation. If a reflex technique is used the radiant energy passes through the heat sensitive copy material whereupon it is absorbed by the characters of the original producing heat which is transmitted to the reproduction material. If a direct transmission technique is used the radiant energy is focused on the original (printed only on one side), the characters of which absorb the energy, convert it to heat, and cause the formation on the copy material of characters duplicating the characters of the original. The heat transferred to the copy material initiates a chemical reaction on the treated sheet leading to the formation of highly colored bodies.

The subject thermographic reproduction process can be used in combination with the processes described in copending applications Serial No. 181,091 and Serial No. 185,347. In this instance, the base would be coated either with an organic, aromatic polyhydroxy or polyamine compound and/or with an aldehyde, a ketone, or an aldehyde-forming compound, or with a solution of a carbohydrate such as lactose, glucose, mannose, etc.

The aromatic polyhydroxy sulfonic acids that are used in the subject process can include compounds such as hydroquinone sulfonic acid, resorcinol sulfonic acid, phloroglucinol sulfonic acid, diresorcinol sulfonic acid, pyrogallol sulfonic acid, naphthol sulfonic acid, catechol sulfonic acid, etc. The sulfonic acid is applied to the reproduction material in the form of a solvent solution at concentrations of from 2% up to 20% and more. Suitable solvents include lower alcohols such as ethanol, isopropanol, butanol, ethyl Cellosolve, benzene, toluene, water, etc. On drying, a tackfree, highly heat-sensitive base is obtained.

The invention is illustrated in the attached schematic drawing in which:

FIGURE 1 is an enlarged fragmentary cross-section of a sheet of reproduction paper embodying the invention and shown in print making relation to a cross-section of the original to be copied; and

FIGURE 2 is an enlarged fragmentary cross-section of a sheet of reproduction material which illustrates a modified process which may be practiced in carrying out the subject invention.

The reproduction or copy material 1 illustrated in the drawing is composed of a sensitive layer 2 of a base 3. The sensitive layer 2 consists of paper which has been treated with a solution containing an organic, aromatic polyhydroxy sulfonic acid. In another embodiment of the invention the sensitive layer can also contain a carbohydrate such as mannose, glucose, etc., or an organic, aromatic polyhydroxy or polyamine compound along with an aldehyde, an aldehyde-forming compound, or a ketone. It is also preferable to incorporate a stabilizing agent in the sensitive layer.

FIG. 1 illustrates a front printing process which constitutes a preferred embodiment of the invention. In this process, the sheet of reproduction material 1 containing sensitized layer 2 on base 3 is superimposed on master or original 4 forming an exposure sandwich S. The master consists of a sheet or base layer 5 of paper or graphically markable sheet material containing a design, drawing, written or typed character 6 to be copied. As is indicated in the figure, character 6 can be on both sides of the sheet in the front printing system. Radiations *Re* such as visible light in the orange and red spectral zones as well as invisible infrared radiation is produced by radiation source 7. The radiations *Re* pass through the copy material 1 and strike the face surface 8 of original 4. Radiation striking character 6 of master 4 are converted to heat which is conducted as indicated at H to the sensitive layer 2 of the reproduction material. An image 6″ is produced which duplicates original character 6. Radiations that are not absorbed either are reflected as shown at 9 or are transmitted through the materials. Where the original is printed on both sides, the unabsorbed radiations are reflected by adjusting radiations *Re*. The radiations are focused on the surface of the copy paper in an elongated zone normal to the face of the sandwich, while the sandwich moves with respect to said zone in the direction of the arrow. If it is desired, the base 3 can be coated or sensitized on both sides. Under these circumstances, the print would appear both on the front and the back of the copy sheet.

In FIG. 2 a back printing method is described in which reproduction material 1 is beneath master or original 4. Once again, the master consists of a sheet or base layer 5 of paper or graphically markable sheet material containing a design, drawing, written or typed character 6 to be copied. The master is superimposed on the sheet of reproduction material 1 to form an exposure sandwich S. Radiations *Re* such as visible light in the orange and red spectral zones as well as invisible infrared radiation is produced by radiation source 7. The radiant energy source 7 preferably is arranged so as to scan the original and copy materials. Radiations *Re* are concentrated and focused on the face surface 8 of the original in an elongated zone normal to the face of the drawing, while the sandwich moves with respect to said zone in the direction of the arrow. As each portion of the sandwich passes through the focal zone, radiations are absorbed by the design area 6 and are converted to heat, which, as shown at H, is conducted through the base 5 of the original 4, to the sensitive layer 2 of the copy material. The heat produces a color-forming reaction in the sensitive layer which produces duplicate characters 6″.

The radiations which are not absorbed by character 6 are reflected as is illustrated at 9, or they may be transmitted through base 5 of the original depending upon the materials used. These rays normally do not affect the reproduction if the original contains a design only on its face surface.

It is preferred that a stabilizing agent be added to the subject treating solution. Materials that can be used as stabilizing agents include urea, biuret, triethanolamine, triphenylphosphate, tributylphosphate, tricresylphosphate, symmetrical dimethyl urea, symmetrical diphenyl urea, thiourea, allyl thiourea, dithiobiuret, and dimethylol urea. The amount of stabilizing agent which can be used in the process can vary from about 0 to about 0.2 gram, and preferably from .02–.08, per gram of the organic, aromatic polyhydroxy sulfonic acid compound.

The following examples are illustrative of the subject invention.

Example I

In this example, reproduction paper having a visible light transmission characteristic of greater than 30% was treated with a composition made up of the following ingredients:

	Grams
Isopropanol (99%)	50.00
Pyrogallol sulfonic acid	2.00
Thiourea	0.05

The solution was applied to the paper with a solution-wet roller, although other means could be used such as spraying, kiss coating, slot fountain, etc. A sufficient amount of solution was applied so that 2.0 grams of acid was present per square yard of paper. After the excess was removed the paper was dried in a drying oven held at about 60 to 80° C. and was superimposed on an original containing typed graphic characters. The resultant sandwich was placed beneath an infrared bulb whereby the characters on the original were reproduced on the copy paper by a front printing system such as is illustrated in FIG. 1 of the drawing. An excellent reproduction of the original was obtained by this method. The characters of the original were black to violet-brown in color.

Example II

In this example, reproduction material was treated with a composition made up of the following ingredients:

	Grams
Butanol	50.00
Resorcinol sulfonic acid	8.00
Symmetrical dimethyl urea	0.15

In this test the solution again was applied to the paper with a solution-wet roller. After the excess had been removed the paper was dried in an oven. A tackfree, highly heat-sensitive base was obtained. The treated paper was placed in sandwich relationship with a superimposed original containing typed graphic characters which were black in color. The sandwich was placed beneath an infrared bulb whereby radiation from the bulb was absorbed by the graphic characters on the original. Heat was transferred to the copy paper which caused a reaction to occur on the treated base forming characters which duplicated the characters of the original. The reproduction had good contrast and was satisfactory in all respects.

Example III

In this example, cellulosic reproduction paper was treated with a composition made up of the following ingredients:

	G.
Toluene	50.00
Catechol sulfonic acid	6.00
Pyrogallol	5.00
Biuret	0.1

Once again, the solution was applied to paper with a solution-wet roller. After the excess was removed the paper was dried in a drying oven held at 60 to 80° C.

and was superimposed on an original containing typed graphic characters. The resultant sandwich was placed beneath an infrared bulb whereby the characters on the original were reproduced on the copy paper by a front printing system such as is described in FIG. 1 of the drawing. The combination of the polyhydroxy sulfonic acid and the aromatic polyhydroxy compound produced excellent characters which duplicated the characters of the original.

Example IV

In this example, reproduction paper was treated with a composition made up of the following ingredients:

	G.
Water	50.00
Phloroglucinol sulfonic acid	2.00
Mannose	5.00
Biuret	0.06

In this test, the solution was applied to paper by a roller, the excess was removed, and the paper was dried in the manner described above. Placing the treated paper beneath a superimposed original containing type graphic characters produces a sandwich which its then placed beneath an infrared bulb. The radiations from the infrared are absorbed by the graphic characters of the original. The heat which is transferred to the copy paper causes a polymerization reaction to occur forming characters which duplicate the characters of the original.

The substitution of an aldehyde such as benzaldehyde, a ketone such as methyl ethyl ketone, and a compound which forms an aldehyde under the conditions of the reaction such as eugenol, for mannose in the composition set forth in Example IV, produced copy paper which provided excellent reproductions. The copy paper could be used either in a reflex system or a direct transmission system.

The reducing carbohydrates which can be used in the invention include monosaccharides such as galactose, glucose, mannose, gulose, dextrose, etc.; oligosaccharides such as maltose, lactose, cellobiose, etc.; polysaccharides, cellulose, starch, dextrin, pentoses such as arabinose, ribose, xylose, and lyxose, etc., and ketose sugars such as fructose. These carbohydrates act in much the same manner as the cellulose of the paper when treated with the particular acid solution and when heated by radiant energy in the manner described above once it has been broken down to a saccharide. The carbohydrates form cyclic aldehyde compounds which polymerize and react with the acid and the organic, aromatic polyhydroxy or polyamine compound to form color bodies. Additionally, certain oxidation side reactions take place producing other color bodies such as humines.

Both aliphatic and aromatic aldehydes and ketones can be used in the invention. It is essential, however, that the aldehydes and ketones have a boiling point of 50° C. or higher. Among the suitable aliphatic aldehydes are those containing from 3 to 8 carbon atoms, such as glyoxal, adipaldehyde, α-hydroxyadipaldehyde, n-butyraldehyde, isobutyraldehyde, valeraldehyde, isovaleraldehyde, trimethylacetaldehyde, n-caproic aldehyde, heptaldehyde, and n-caprylic aldehyde. Suitable aliphatic ketones would include those containing from 4 to 11 carbon atoms, such as dihydroxy acetone, methyl ethyl ketone, diethyl ketone, methyl propyl ketone, methyl isopropyl ketone, methyl n-butyl ketone, methyl isobutyl ketone, methyl sec-butyl ketone, ethyl propyl ketone, ethyl isopropyl ketone, dipropyl ketone, methyl amyl ketone, dibutyl ketone, and diamyl ketone. Suitable aromatic aldehydes and ketones would include benzaldehyde, ortho-, meta- and para-toluic aldehyde, ortho-, meta- and para-hydroxy benzaldehyde, ortho-, meta-, and para-chlorobenzaldehyde, ortho- and meta-nitrobenzaldehyde, α-naphthaldehyde, phenylacetaldehyde, vanillin, anisaldehyde, salicylic aldehyde, acetophenone and benzophenone. Among the compounds which form aldehydes under the conditions of the reaction which can be used in the process are eugenol, isoeugenol, anethole, and safrole.

As was indicated above, the solvent solution can contain from 2% to more than 20% (for example, 30%) of organic, aromatic polyhydroxy sulfonic acid.

The temperature of the paper in the areas of the polymerization or character producing reaction will vary from about 240° F. to about 360° F. The temperature required to produce a satisfactory print, of course, will depend upon the printing speed, the voltage across the lamp source, etc. In most instances, the paper need be exposed to the radiation for only a brief period of time, for example, from 0.05 second up to about 3 seconds, and preferably from 0.1 to 0.5 second.

In carrying out the subject process, it is not necessary to use binder resins to hold the applied coatings to the surface of the base. If it is desired, however, water-soluble or water-emulsifiable polymers can be used such as polyvinyl acetates, acrylic type polymers, polyvinyl acetate-acrylic type copolymers, water-soluble alkyd resins, water-soluble polyesters, water-soluble alkyd-copolymers, etc.

The reproduction paper that is used in the subject process should have light transmitting characters such that at least 30% visible light or infrared radiations pass through the paper. In addition to paper other materials having the ability to transmit this much light can be used in the process. Such materials would include Mylar, glass cloth, glassine papers.

The amount of organic, aromatic polyhydroxy sulfonic acid that is used in the process can vary widely. It has been found that from 1 to about 4 grams of acid per square yard of paper will suffice in most instances. In a preferred embodiment from 1.5 to 2.5 grams of organic, aromatic polyhydroxy sulfonic acid are used per square yard of paper.

Obviously many modifications and variations of the invention as hereinbefore set forth may be made without departing from the spirit and scope thereof and, therefore, only such limitations should be imposed as are indicated in the appended claims.

We claim:

1. A process for graphically reproducing an original which comprises: placing an original having preferential radiation absorbing areas in contact with a cellulosic paper base coated with a visibly heat-sensitive composition, said composition containing an aromatic polyhydroxy sulfonic acid compound, and thereafter irradiating said original with heat producing radiations to effect a reaction in the areas of said supported layer registering with said radiation absorbing areas, whereby said original is visibly reproduced, the amount of acid coated on said base being from about 1 to about 4 grams per square yard.

2. A process for graphically reproducing an original which comprises: placing an original having preferential radiation absorbing areas in contact with a paper coated with a visibly heat-sensitive composition, said composition comprising an aromatic polyhydroxy sulfonic acid compound and a carbohydrate selected from the group consisting of a monosaccharide, an oligosaccharide, a polysaccharide, a pentose, and a ketose sugar, and irradiating said original with heat producing radiations to effect a reaction in the areas of said supported layer registering with said radiation absorbing areas whereby said original is visibly reproduced, the amount of acid coated on said base being from about 1 to about 4 grams per square yard.

3. A process for graphically reproducing an original which comprises: placing an original having preferential radiation absorbing areas in contact with a cellulosic paper base coated with a visibly heat-sensitive composition, said composition comprising an aromatic polyhydroxy sulfonic acid compound and a compound selected

from the group consisting of an aldehyde having a boiling point greater than 50° C., a ketone having a boiling point greater than 50° C., eugenol, isoeugenol, anethole, and safrole, and irradiating said original with heat producing radiations to effect a reaction in the areas of said supported layer registering with said radiation absorbing areas whereby said original is visibly reproduced, the amount of acid coated on said base being from about 1 to about 4 grams per square yard.

4. Reproduction material which comprises: a cellulosic paper base coated with a composition containing an aromatic polyhydroxy sulfonic acid, the amount of said acid being from about 1 to about 4 grams per square yard of base.

5. Reproduction material which comprises: a paper base coated with a composition containing an aromatic polyhydroxy sulfonic acid and a reducing type carbohydrate selected from the group consisting of a monosaccharide, an oligosaccharide, a polysaccharide, a pentose, and a ketose sugar, the amount of said acid being from about 1 to about 4 grams per square yard of base.

6. Reproduction material which compirses: a paper base coated with a composition containing an aromatic polyhydroxy sulfonic acid and a compound selected from the group consisting of an aldehyde having a boiling point greater than 50° C., a ketone having a boiling point greater than 50° C., eugenol, isoeugenol, anethole, and safrole, the amount of said acid being from about 1 to about 4 grams per square yard of said base.

7. A process for producing a thermally developable copy sheet which comprises: applying a solvent solution of an aromatic polyhydroxy sulfonic acid compound to a cellulosic paper base, the amount of said polyhydroxy sulfonic acid compound being from about 2% to about 30% based on the weight of the solvent, said reproduction paper having light and infrared transmittant characteristics such that at least 30% of the radiations pass through said paper, the amount of said acid being from about 1 to about 4 grams per square yard of said paper base.

8. A process for producing a thermally developable copy sheet which comprises: applying a solvent solution of an aromatic polyhydroxy sulfonic acid compound and a reducing type carbohydrate selected from the group consisting of a monosaccharide, an oligosaccharide, a polysaccharide, a pentose, and a ketose sugar to a cellulosic paper base, the amount of said polyhydroxy sulfonic acid compound and reducing type carbohydrate being from about 2% to about 30% based on the weight of the solvent, said reproduction paper having light and infrared transmittant characteristics such that at least 30% of the radiations pass through said paper, the amount of said acid coated on said paper base being from about 1 to about 4 grams per square yard of said base.

9. A process for producing a thermally developable copy sheet which comprises: applying a solvent solution of an aromatic polyhydroxy sulfonic acid compound and a compound selected from the group consisting of an aldehyde having a boiling point greater than 50° C., a ketone having a boiling point greater than 50° C., eugenol, isoeugenol, anethole, and safrole to a cellulosic paper base, the amount of said polyhydroxy sulfonic acid compound and compound selected from the group consisting of an aldehyde, a ketone, and an aldehyde-forming compound being from about 2% to about 30% based on the weight of the solvent, said reproduction paper having light and infrared transmittant characteristics such that at least 30% of the radiations pass through said paper, the amount of said acid coated on said paper base being from about 1 to about 4 grams per square yard of said base.

10. A process as in claim 1 wherein said aromatic polyhydroxy sulfonic acid is selected from the group consisting of hydroquinone sulfonic acid, resorcinol sulfonic acid, phloroglucinol sulfonic acid, diresorcinol sulfonic acid, pyrogallol sulfonic acid, naphthol sulfonic acid, and catechol sulfonic acid.

11. A process as in claim 2 wherein said aromatic polyhydroxy sulfonic acid is selected from the group consisting of hydroquinone sulfonic acid, resorcinol sulfonic acid, phloroglucinol sulfonic acid, diresorcinol sulfonic acid, pyrogallol sulfonic acid, naphthol sulfonic acid, and catechol sulfonic acid.

12. A process as in claim 3 wherein said aromatic polyhydroxy sulfonic acid compound is selected from the group consisting of hydroquinone sulfonic acid, resorcinol sulfonic acid, phloroglucinol sulfonic acid, diresorcinol sulfonic acid, pyrogallol sulfonic acid, naphthol sulfonic acid, and catechol sulfonic acid.

13. Reproduction material which comprises: a cellulosic paper base coated with a composition containing an aromatic polyhydroxy sulfonic acid selected from the group consisting of hydroquinone sulfonic acid, resorcinol sulfonic acid, phloroglucinol sulfonic acid, diresorcinol sulfonic acid, pyrogallol sulfonic acid, naphthol sulfonic acid, and catechol sulfonic acid, the amount of said acid being from about 1 to about 4 grams per square yard of said paper base.

14. Reproduction material which comprises: a cellulosic paper base coated with a composition containing an aromatic polyhydroxy sulfonic acid selected from the group consisting of hydroquinone sulfonic acid, resorcinol sulfonic acid, phloroglucinol sulfonic acid, diresorcinol sulfonic acid, pyrogallol sulfonic acid, naphthol sulfonic acid, and catechol sulfonic acid, and mannose, the amount of said acid being from about 1 to about 4 grams per square yard of said paper base.

15. A process as in claim 7 wherein said aromatic polyhydroxy sulfonic acid compound is selected from the group consisting of hydroquinone sulfonic acid, resorcinol sulfonic acid, phloroglucinol sulfonic acid, diresorcinol sulfonic acid, pyrogallol sulfonic acid, naphthol sulfonic acid, and catechol sulfonic acid.

16. A process as in claim 8 wherein said aromatic polyhydroxy sulfonic acid compound is selected from the group consisting of hydroquinone sulfonic acid, resorcinol sulfonic acid, phloroglucinol sulfonic acid, diresorcinol sulfonic acid, pyrogallol sulfonic acid, naphthol sulfonic acid, and catechol sulfonic acid.

17. A process as in claim 9 wherein said aromatic polyhydroxy sulfonic acid compound is selected from the group consisting of hydroquinone sulfonic acid, resorcinol sulfonic acid, phloroglucinol sulfonic acid, diresorcinol sulfonic acid, pyrogallol sulfonic acid, naphthol sulfonic acid, and catechol sulfonic acid.

References Cited in the file of this patent

UNITED STATES PATENTS

1,844,199	Bicknell et al.	Feb. 9, 1932
1,944,293	Martinez	Jan. 23, 1934
2,625,494	Morrison	Jan. 13, 1953
2,844,733	Miller et al.	July 22, 1958
2,910,377	Owen	Oct. 27, 1959
3,024,362	Sus et al.	Mar. 6, 1962