United States Patent

[11] 3,619,356

[72] Inventor **James L. Keen**
New Brighton, Minn.

[21] Appl. No. **715,544**
[22] Filed **Mar. 25, 1968**
[45] Patented **Nov. 9, 1971**
[73] Assignee **General Mills, Inc.**

[54] **FIXING OF ANIONIC DYESTUFFS TO CELLULOSIC FIBERS WITH CATIONIC POLYMERIC FATTY ACID POLYALKYLENE POLYAMINES**
17 Claims, No Drawings

[52] **U.S. Cl.** **162/162,** 8/7, 8/85, 8/100, 162/179, 162/182, 260/583
[51] **Int. Cl.** **D21h 3/80**
[50] **Field of Search** ..... 162/179, 182, 162, 183, 181; 8/7, 85, 100; 260/583 I

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Dyeing and Chemical Technology of Textile Fibers

Primary Examiner—S. Leon Bashore
Assistant Examiner—Richard H. Anderson
Attorneys—Anthony A. Juettner, William C. Babcock and Gene O. Enockson

ABSTRACT: Cellulosic fibers are dyed by treatment with an anionic dye such as Calcocid Blue 2G (a tri-phenyl methane dye, color Index 42090) and a polyamine derived from polymeric fat acids such as the polyamine obtained by hydrogenating, in the presence of ammonia, the reaction product of ammonia and tall oil fatty acids. Paper is prepared by adding such dye and polyamine to the aqueous fiber dispersion prior to the formation of sheets.

FIXING OF ANIONIC DYESTUFFS TO CELLULOSIC FIBERS WITH CATIONIC POLYMERIC FATTY ACID POLYALKYLENE POLYAMINES

The present invention relates to a process of dyeing cellulosic fibers and to the resulting product. In one specific aspect, it particularly relates to the production of colored paper from cellulosic fibers wherein an anionic dye is used in combination with a polyamine derived from polymeric fat acids.

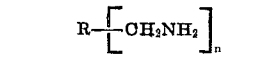
Perhaps the most used procedure for preparing colored paper is to add a dye to the paper while it is still in the fibrous state—i.e. prior to being formed on the machine. Such procedure is commonly referred to as "beater dyeing." The open top and vigorous mixing action of the beater makes it an excellent place to add the dyes. However, the term "beater dyeing" is taken to include also dyeing in Hydropulpers, Dynopulpers, Jordans mixing chests, mixing tanks, fan pumps, head boxes and the like where similar mixing conditions exist.

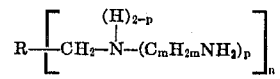
The main classes of dyes used in the production of colored papers using beater dyeing are the acid, direct and basic dyes. The first two classes, namely the acid and direct dyes, are anionic in nature and are generally sodium salts of color acids. They are water soluble and are available in practically all shades of the rainbow. The acid dyes have little, if any, affinity for cellulose. Accordingly, they have most commonly been employed where the furnish also contains alum or both alum and rosin.

I have now discovered that the retention of anionic dyes by cellulosic fibers can be improved if the fibers are treated with a combination of the anionic dye and a polyamine derived from a polymeric fat acid. My process has particular application to the dyeing of cellulosic fibers with acid dyes. However, it is also of value when other anionic dyes such as the direct dyes are to be used. While these latter materials have affinity for cellulosic fibers, the dyeing intensity can be increased with the use of polymeric fat acid based polyamines and the amount of the direct dyes needed to produce a certain color may be reduced. It is theorized that the polyamines employed are in some way held by the fibers and yet are capable of complexing or reacting with the anionic dyes to also hold same to an increased degree to the fibers. The process is especially valuable in dyeing the cellulosic fibers prior to their formation into sheets although it is also useful in dyeing already formed sheets of paper as well as fabrics and the like derived from cellulosic fibers such as cotton.

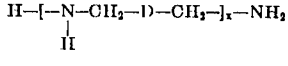
As indicated, the anionic dye and polymeric fat acid based polyamine are preferably added to dilute dispersions of the cellulosic fibers prior to the formation of sheets from such dispersions. Preferably, the addition is made to the beater or refiner or to the already beaten or refined fiber. In the latter case, the dye and polyamine are thoroughly mixed with the beaten or refined fibers. Any of the wide variety of commercially available beaters and/or refiners can be used. The cellulosic fibers can be any of those used in papermaking, such as those commonly referred to as sulfite, soda, sulfate and ground wood stock, or fibers derived from rag, cotton, bast, flax and stem fibers such as straw, or from repulped broke. The fibers may be bleached or unbleached. The concentration of the fibers in the aqueous dispersion is generally less than about 4.0 percent by weight and preferably in the range of 0.5 to 3.0 percent by weight.

The polymeric fat acid based polyamines useful in the present invention are those having at least one polymeric fat acid radical and at least two primary amine groups. The preferred amines are those having the following formulae:

(I) 

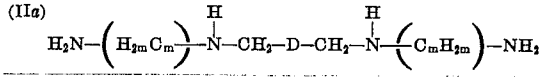
(II) 

and

(III) 

where *n* is an integer of 2 to about 4, *m* is an integer of 3 or 4, *p* is an integer of 1 or 2, *x* is an integer of 2 to about 40 or higher, R is the polyvalent hydrocarbon radical of a polymeric fat acid and D is the divalent hydrocarbon radical of dimeric fat acid. Especially preferred compounds of the first two formulae are those wherein *n* is 2. Such amines have the following formulae:

(Ia) 

(IIa) 

where *m* and D are as above defined.

As indicated all of such polyamines are derived from polymeric fat acids. Such polymerized fat acids are prepared by polymerizing ethylenically unsaturated monobasic carboxylic acids having 16 to 22 carbon atoms or the lower alkyl esters thereof. The preferred aliphatic acids are the mono and polyolefinically unsaturated 18 carbon atom acids. Representative octadecenoic acids are 4-octadecenoic, 5-octadecenoic, 6-octadecenoic (petroselinic), 7-octadecenoic, 8-octadecenoic, cis-9octadecenoic (oleic), trans-9-octadecenoic (elaidic), 11-octadecenoic (vaccenic), 12-octadecenoic and the like. Representative octadecadienoic acids are 9,12-octadecadienoic (linoleic), 9,11-octadecadienoic, 10,12-octadecadienoic, 12,15-octadecadienoic and the like. Representative octadecadienoic acids are 9,12,15-octadecatrienoic (linolenic), 6,9,12-octadecatrienoic, 9,11,13-octadecatrienoic (eleostearic), 10,12,14-octadecatrienoic (pseudoeleostearic) and the like. A representative 18 carbon atom acid having more than three double bonds is moroctic acid which is indicated to be 4,8,12,15-octadecatetraienoic acid. Representative of the less preferred (not as readily available commercially) acids are: 7-hexadecenoic, 9-hexadecenoic (palmitoleic), 9-eicosenoic (gadoleic), 11-eicosenoic, 6,10,14-hexadecatrienoic (hiragonic), 4,8,12,16-eicosatetraenoic, 4,8,12,15,18-eicosapentanoic (timnodonic), 13-docosenoic (erucic), 11-docosenoic (cetoleic), and the like.

The ethylenically unsaturated acids can be polymerized using known catalytic or noncatalytic polymerization techniques. With the use of heat alone, the mono-olefinic acids (or the esters thereof) are polymerized at a very slow rate while the polyolefinic acids (or the esters thereof) are polymerized at a reasonable rate. If the double bonds of the polyolefinic acids are in conjugated positions, the polymerization is more rapid than when they are in the nonconjugated positions. Clay catalysts are commonly used to accelerate the dimerization of the unsaturated acids. Lower temperatures are generally used when a catalyst is employed.

The polymerization of the described ethylenically unsaturated acids yields relatively complex products which usually contain a predominant portion of dimerized acids, a smaller quantity of trimerized and higher polymeric acids and some residual monomers. The dimerized acids having 32 to 44 carbon atoms can be obtained in reasonably high purity from the polymerization products by vacuum distillation at low pressures, solvent extraction or other known separation procedures. The polymerization product varies somewhat depending on the starting fat acid or mixture thereof and the polymerization technique employed—i.e. thermal, catalytic, particular catalyst, conditions of pressure, temperature, etc. Likewise, the nature of the dimerized acids separated from the polymerization product also depends somewhat on these factors although such acids are functionally similar.

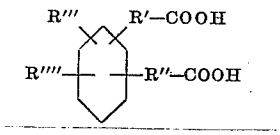
Analysis of dimerized acids prepared from linoleic acid rich starting materials using heat alone or heat plus a catalyst, such as an acid or alkaline clay, shows that the product contains structurally similar acids having monocyclic tetra-substituted ring structures as well as acids with two and three rings, such additional rings generally being fused to the six carbon atom ring. The clay catalyzed dimerized acids have been shown to contain some aromatic rings according to ultraviolet and infrared spectroscopy. These aromatic rings are believed to be formed by hydrogen transfer (by catalytic action of clay) from a substituted cyclohexene ring to form a substituted benzene

ring. Polymerization of pure oleic acid using a clay catalyst has been shown to yield a mixture of dimerized fat acids of which approximately 25–30 percent by weight have a one ring cyclic structure with the remainder being noncyclic. However, when mixtures of oleic and linoleic acids (such as from tall oil) are polymerized, the resulting dimerized fat acid contains little if any dimer having a noncyclic structure.

It is apparent from the above and other published analyses that the polymerization of the ethylenically unsaturated acids yields complex products. The dimer fraction thereof, generally consisting of a mixture of acids, can be assigned the formula:

HOOC–D – COOH

where D is a divalent hydrocarbon group containing 30 to 42 carbon atoms. It is also apparent that said divalent hydrocarbon group is complex since a mixture of acids normally results from the polymerization and subsequent fractionation. These acids have structural and functional similarities. Thus such mixture of acids contains a significant proportion of acids having a six carbon atom ring (about 25 percent or more even when the starting fat acid is a mono-olefinically unsaturated acid such as oleic). The remaining carbon atoms in the divalent hydrocarbon group of such ring containing acids are then divided between divalent and monovalent radicals which may be saturated or ethylenically unsaturated. Such radicals may form one or more additional cyclic structures which are generally fused to the first six membered ring. Many of such dimeric acids may be considered as having a theoretical idealized, general formula as follows:



where R′ and R″ are divalent hydrocarbon radicals, R‴ and R⁗ are monovalent hydrocarbon radicals and the sum of the carbon atoms in R′–R⁗ is 24 –36. The ring may be saturated or it may contain one to three double bonds depending on the specific starting material, polymerization conditions and subsequent treatment including hydrogenation. It is also understood that the R′–R⁗ radicals may form one or more additional cyclic structures which are generally fused to the first ring.

As a practical matter, the dimeric fat acids are preferably prepared by the polymerization of mixtures of acids (or the simple aliphatic alcohol esters—i.e. the methyl esters) derived from the naturally occurring drying and semidrying oils or similar materials. Suitable drying or semidrying oils include soybean, linseed, tung, perilla, oiticia, cottonseed, corn, sunflower, dehydrated castor oil and the like. Also, the most readily available acid is linoleic or mixtures of the same with oleic, linolenic and the like. Thus, it is preferred to use as the starting materials, mixtures which are rich in linoleic acid. An especially preferred material is the mixture of acids obtained from tall oil which mixture is composed of approximately 40–45 percent linoleic and 50–55 percent oleic. It is also preferred to carry out the polymerization in the presence of a clay. Partial analysis of a relatively pure dimer fraction (98.5 percent dimer) obtained from the product prepared by polymerizing the tall oil fatty acids in the presence of 10 percent by weight of an alkaline montmorillonite clay at a temperature of 230° C. and a pressure of 140 p.s.i. for 5 hours showed that it was a mixture of C_{36} acids, the major proportion thereof being monocyclic of the above general formula with a substantial amount of the acids having a ring containing three double bonds (aromatic) and saturated side chains. Such mixture of acids was used in the preparation of the dinitrile and thence the various polyamines used in the examples to follow. It is also to be understood that the corresponding hydrogenated dimeric fat acids are useful in preparing the dinitriles and ultimately the polyamines employed in the present invention.

The polymerized fat acids are converted to the corresponding polynitriles by reaction with ammonia under nitrile forming conditions. The details of this reaction are set forth in Chapter 2 of "Fatty Acids and Their Derivatives" by A. W. Ralston, John Wiley & Sons, Inc., New York (1948).

The polyamines of the formulae (I.) and (Ia.) above are then prepared by hydrogenating the polynitriles in the presence of ammonia. Polyamines of this type are commercially available materials. Their preparation is further described in McCaleb et al. Pat. No. 3,010,782 which disclosure is incorporated herein by reference.

Polyamines of the formulae (II.) and (IIa.) are also commercially available. Such polyamines are prepared by reacting the compounds of formulae (I.) and (Ia.) with an unsaturated nitrile such as acrylonitrile, crotononitrile, and methacrylonitrile and then catalytically reducing the resulting polynitrile. The preparation of these compounds are also further described in the above-identified McCaleb et al. patent.

The polyamines of the formula (III.) are prepared by the condensation polymerization of the dinitriles under secondary-amine-forming conditions. Typical reaction conditions utilize hydrogen pressures in the range of 25 to 1000 p.s.i.g. at temperatures in the range of 200 to 290° C. The preparative reaction is illustrated by the following equation:

$$NC{-}D{-}CN \xrightarrow[Cat.]{H_2} H{-}[{-}N(H){-}CH_2{-}D{-}CH_2{-}]_x{-}NH_2 + NH_3\uparrow$$

The ammonia byproduct is swept from the reaction mixture with hydrogen gas. Various of these polyamines are also commercially available and their preparation is further described in Vertnik Pat. No. 3,217,028 which disclosure is incorporated herein by reference.

The polyamines derived from the polymeric fat acids are used in an amount sufficient to increase the retention of the anionic dyes on the fibers. Preferably, the polyamines are used in an amount of about 0.05 to 1.0 percent by weight based on the dry weight of the fibers.

Any of a wide variety of anionic dyes can be used in the present invention. Typical of such dyes are the following acid dyes: Nigrosine 02P, Nigrosine OPX Dustless, Nigrosine J, Acid Blue R, Acid Blue B, Acid Blue 2R, Acid Blue 3B, Quinizol Blue BP, Bond Blue B Conc., Acid Green 2G Conc. Dustless, Acid Orange Y Dustless, Acid Green Extra Conc., Acid Orange RR Dustless, Azo Scarlet Y Extra Conc., Crocein Scarlet MOO Conc. Dustless, Crocein Scarlet MOON, Serisine B, Fast Red Conc., Acid Carminette, Fast Acid Carminette SC, Metanil Yellow MXXX Conc. Dustless, Acid Violet 4BNS Dustless, Acid Violet 6B Conc., Chinoline Yellow W Conc. and the like. These and other acid and direct dyes are disclosed in "Dyestuff Data for Paper Makers," American cyanamid Company, 1952, pp. 17–21 and 25–30 and in "University of Maine Lectures on Pulp and Paper Manufacture," 1950, pp. 241–245, the disclosures of which are incorporated herein by reference.

The amount of dye added to the cellulosic fiber is not critical and, of course, depends on the strength of the dye and paper color desired. Preferably the dye is used in an amount of about 0.05 to 1.0 percent by weight based on the dry weight of the fibers.

The anionic dye is preferably added to the fiber in the form of a dilute aqueous solution or dispersion. Likewise, the polyamine is also preferably added in the form of a dilute aqueous solution or dispersion. Solubilization of the polyamine can be effected by at least partially neutralizing the same with a water soluble organic or inorganic acid such as acetic acid and mineral acids including hydrochloric, sulfuric and the like. The use of the dilute solutions or dispersions of dye and polyamine results in a more even distribution thereof on the fibers. It is also preferred that the said solutions or dispersions contain less than about 10 percent by weight of the polyamine and/or dye. In many instances, it is preferred that

the polyamine is first added to the fibers followed by addition of the anionic dye. Where the materials are added to already formed sheets or fabrics derived from cellulosic fibers, the polyamine solution or dispersion is also first preferably applied. In papermaking, such addition can take place at the calendar. But generally, any method of dipping, spraying, etc. of the sheets or fabrics can be employed.

In the preferred procedure wherein the polyamine derived from polymeric fat acids and the anionic dye are thoroughly mixed with an aqueous pulp or fiber dispersion, sheets can then be prepared using conventional techniques. In this respect, the relatively uniform dispersion of the pulp fibers containing the anionic dye and the polyamine is filtered through a screen which leaves a wet sheet on the screen. This sheet can then be dried and otherwise processed to make paper which can be used for a variety of purposes including use as a nonwoven fabric. Any of the commercially available forming machines can be used including the Fourdrinier and cylinder machines. The wet sheets are preferably dried at temperatures of 200° F. to 250° F. to a moisture content of less than about 10 percent. Any conventional drying technique can be used such as steam heated dryers.

It is also to be understood that conventional additives such as fillers and the like can be added. Representative fillers are talc, $CaCO_3$, silica, TiO_2 and so forth.

The following examples further illustrate and describe the process and products of the present invention and are not to be considered as limiting. Unless otherwise indicated all parts and %'s are by weight.

EXAMPLE I

One liter samples of an aqueous dispersion of moderately refined, bleached Kraft pulp at 0.8 percent solids at the pH of local tap water (about 7.9) were first prepared. To one sample was added 15 cc. of a 0.2 percent aqueous solution of the acid dye Calcocid Blue 2G (a tri-phenyl methane dye, Color Index 42090). To a second sample was added 15 cc. of the dye solution and 4 cc. of a 1 percent aqueous solution of a diamine (1 cc. diamine/100 cc. water containing 0.2 cc. acetic acid) of the formula *Ia.* above derived as indicated from the mixture of C_{36} acids prepared by polymerizing tall oil fatty acids. The dispersions were thoroughly mixed and then single handsheets were made from such pulp samples on a Nobel and Wood Handsheet machine. The wet sheets were dried on a rotary dryer at between 200 to 250° F. until they contained less than about 10 percent moisture. The sheets obtained from the dispersion containing the diamine were of a pretty pastel blue color whereas the sheets obtained from the dispersion containing only the dye were not dyed to any noticeable extent being creamy white.

EXAMPLE II

Handsheets were prepared as in example I except that the diamine was replaced by a polyamine of the formula *IIa.* above wherein *m* is 3 and D is the same as in the diamine of example I. The resulting handsheets had a relatively deep blue color indicating that even more of the dye was retained than with the diamine as used in example I.

EXAMPLE III

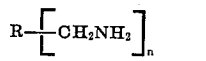
Handsheets were prepared as in example I except that the diamine was replaced by a polyamine of the formula III above wherein *x* is an average of about 6 and D is the same as in the diamine of example I. The resulting handsheets were of substantially the same pretty pastel blue color as those prepared from the diamine containing dispersion of example I.

The embodiments of the invention in which an exclusive property or privilege is claimed as defined as follows:

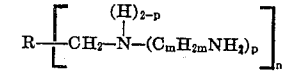
1. The process of dyeing cellulosic fibers which comprises treating such fibers with (1) an aqueous solution of an anionic dye and (2) a polyamine having at least two primary amine groups and at least one polyvalent hydrocarbon group of polymerized fat acids derived from ethylenically unsaturated aliphatic monobasic carboxylic acids of 16 to 22 carbon atoms, said polyamine being used in an amount sufficient to increase the retention of the anionic dye by the fibers.

2. The process of claim 1 where in the polyamine is selected from those of the following formulae:

(I)

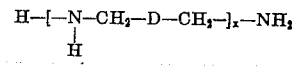


(II)



and

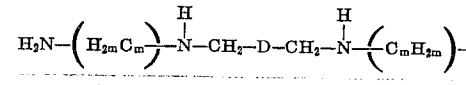
(III)



where *n* is an integer of 2 to about 4, *m* is an integer of 3 or 4, *p* is an integer of 1 or 2, *x* is an integer of at least 2, R is the polyvalent hydrocarbon radical of polymerized fat acids and D is the divalent hydrocarbon radical of dimerized fat acids, said polymerized and dimerized fat acids being derived from ethylenically unsaturated aliphatic monobasic carboxylic acids of 16 to 22 carbon atoms.

3. The process of claim 1 wherein the polyamine has the formula: H_2N-CH_2-D-CH_2-NH_2 where D is the divalent hydrocarbon radical of dimerized fat acids derived from ethylenically unsaturated aliphatic monobasic carboxylic acids of 16 to 22 carbon atoms.

4. The process of claim 1 wherein the polyamine has the formula:



where *m* is an integer of 3 or 4 and D is the divalent hydrocarbon radical of dimerized fat acids derived from ethylenically unsaturated aliphatic monobasic carboxylic acids of 16 to 22 carbon atoms.

5. The process of claim 1 wherein the ethylenically unsaturated aliphatic monobasic carboxylic acids contain 18 carbon atoms.

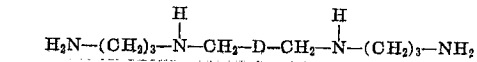
6. The process of claim 5 wherein the 18 carbon atom acids comprise a mixture rich in linoleic acid.

7. The process of claim 1 wherein the polyamine is added to the fibers as an aqueous solution.

8. The process of claim 1 wherein the polyamine is used in an amount of about 0.05 to 1.0 percent by weight based on the dry weight of the fibers.

9. The process of claim 8 wherein the anionic dye is an acid dye.

10. The process of claim 9 wherein the polyamine has the formula:



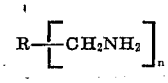
where D is the divalent hydrocarbon radical derived from a mixture of 18 carbon atom ethylenically unsaturated aliphatic monobasic carboxylic acids rich in linoleic acid.

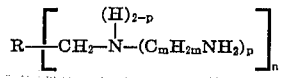
11. In the process of preparing colored paper from an aqueous dispersion of cellulosic fibers and an anionic dye, the improvement comprising adding a polyamine having at least two primary amine groups and at least one polyvalent hydrocarbon group of polymerized fat acids derived from ethylenically unsaturated aliphatic monobasic carboxylic acids of 16 to 22 carbon atoms to the dispersion before forming the dispersion into sheets, said polyamine being used in an amount sufficient to increase the retention of the anionic dye by the cellulosic fibers.

12. The process of claim 11 wherein both the anionic dye and the polyamine are added to the fiber dispersion as dilute

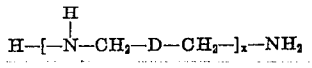
aqueous dispersions or solutions.

13. The process of claim 12 wherein the polyamine is selected from those of the following formulae:

(I) 

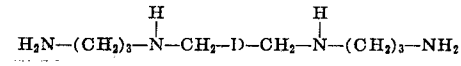
(II) 

and

(III) 

where n is an integer of 2 to about 4, m is an integer of 3 or 4, p is an integer of 1 or 2, x is an integer of at least 2, R is the polyvalent hydrocarbon radical of polymerized fat acids and D is the divalent hydrocarbon radical of dimerized fat acids, said polymerized and dimerized fat acids being derived from ethylenically unsaturated aliphatic monobasic carboxylic acids of 16 to 22 carbon atoms.

14. The process of claim 13 wherein the anionic dye is an acid dye and the polyamine is used in an amount of about 0.05 to 1.0 percent by weight based on the dry weight of the fibers and has the formula



15. The process of claim 14 wherein D is the divalent hydrocarbon radical derived from a mixture of 18 carbon atom ethylenically unsaturated aliphatic monobasic carboxylic acids rich in linoleic acid.

16. The product prepared by the process of claim 1.

17. The paper product prepared by the process of claim 111.

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