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3,368,484

PAPER OFFSET MASTER

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This invention relates to a novel direct image paper offset master and a method for its manufacture. More specifically, the invention pertains to a direct image paper offset master which is coated with a composition containing a relatively undegraded cellulose sulfate having a degree of substitution (D.S.) in the range of 1-3.

The requirements for a direct image paper offset master are quite stringent. The coated surface of the paper must be capable of uniformly accepting ink or other greasy or oily imaging materials so as to give a faithful reproduction of the image, while the non-imaged areas of the paper offset master are kept free of ink by wetting with an etch or fountain solution. In order that the offset master function properly, its surface must be both hydrophilic and oleophilic. Also, the paper coating must be water resistant such that the coating adhesive is not dissolved by contact with water.

An object of this invention is to provide a direct image paper offset master whose surface coating contains a relatively undegraded colloidal cellulose sulfate having a degree of substitution of from 1 to 3, the term degree of substitution having reference to the average number of sulfate substituent groups per unit in the cellulose molecule.

A further object is to provide a method for preparing a direct image paper offset master whose surface coating contains a relatively undegraded colloidal cellulose sulfate having a degree of substitution of from 1 to 3.

Additional objects will become apparent from a reading of the specification and claims which follow.

In forming a direct image paper offset master according to my invention, a suitable paper rawstock is first obtained. The paper sheet must be of a high wet strength and should, therefore, be made of long fibers and be highly sized. In some instances, it may be desirable to pre-coat both sides of the paper with a base coat to provide an essentially insoluble surface thereon. Highly-sized high wet strength papers are well known to the art and do not, in themselves, form a part of my invention. See, for example, the text entitled, "Pulp and Paper," vol. II, by Casey, 2nd ed. (1960), Interscience Publishers, 250 Fifth Ave., New York, N.Y., which discusses the techniques for producing highly sized, long fiber containing paper. Moreover, the pre-coating or surface sizing of paper to provide it with an essentially insoluble surface is also a well known procedure. Many coatings are known which can be employed for this purpose. To illustrate, casein in combination with suitable pigments may be so employed as a coating. Surface coatings or surface sizings are also discussed at length in the Casey text cited previously. The various pigments which may be incorporated in the pre-coating are described in the text entitled "Paper Coating Pigments," Monograph Series—No. 20, by the Technical Association of the Pulp and Paper Industry (TAPPI), 155 E. 44th St., New York 17, N.Y.

The prepared sheet of paper is then coated with a suitable surface coating composition according to my invention. The surface coating composition contains a suitable inert pigment such as various clays, calcium carbonate, titanium dioxide, zinc oxide, and the like, dispersed in an aqueous solution of a water soluble salt of a relatively undegraded cellulose sulfate having a D.S. of 1 to 3. This coating forms the printing surface of the paper offset master. I have found that varying weight ratios of pig-

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ment to cellulose sulfate may be employed in the paper coating. In general, I employ a weight ratio of pigment to cellulose sulfate which may vary from about 10:1 to about 3.33:1. Preferably, however, the ratio of pigment to cellulose sulfate ranges from about 5:1 to about 4:1. The quantity of water employed in the coating composition can be varied depending on the consistency desired. In general, the water constitutes from about 60 to about 85% and preferably about 70 to about 75% by weight of the coating composition. The water soluble cellulose sulfate salts employed are those which in aqueous solution give a pH from in excess of 6 to about 7 or slightly above. The pigments employed in the surface coating may be of the various pigments as set forth in the TAPPI text, above. Generally, the pigment employed in the surface coating is the same as that employed in the pre-coating.

The cellulose sulfate salts which I employ and their method of preparation are described in U.S. patent application, Ser. No. 467,738, filed June 28, 1965 in the name of Richard G. Schweiger and entitled "Process of Preparing a Gellable Colloidal Cellulose Sulfate and Product." U.S. application Ser. No. 467,738 is a continuation-in-part of an earlier application Ser. No. 347,351, filed Feb. 26, 1964. The subject matter of patent application Ser. No. 467,738 is incorporated herein by reference.

In the cellulose sulfate salts employed, the cellulose remains relatively undegraded such that the sulfated material exhibits colloidal properties with a desired degree of substitution. The degree of substitution (D.S.) of the cellulose sulfate is between 1.0 and 3.0. The preparation of the cellulose sulfate employed in my invention is accomplished by first forming a complex of sulfur trioxide and a lower N-dialkyl amide, which is used as a sulfating reagent for the cellulose. Prior to the sulfation reaction, the cellulose is preferably admixed or diluted with at least an equal weight of the same lower N-dialkyl amide employed in the complex. Preferably, the N-dialkyl amide is dimethyl formamide although diethyl formamide, dimethyl acetamide, diethyl acetamide, and dimethyl piperonamide may also be used.

As described in U.S. patent application, Ser. No. 467,738, the cellulose sulfate which I employ has a D.S. of 1 to 3. The D.S. can range in excess of 2.0 and is preferably in the range of 1.5 to 2.6. The cellulose sulfate is soluble in water and forms gels when potassium ions are added to aqueous solutions of the cellulose sulfate. The cellulose sulfate which I employ, when added to water, produces viscosities in excess of 20 cps. at a concentration of 1% by weight as measured by a Brookfield Synchro Electric Viscometer, Model LVF, at 60 r.p.m. and a temperature of 25° C., and, as shown in the examples of application Ser. No. 467,738, the viscosities range upwardly in excess of 100 cps. to as high as 500 cps. at a 1% concentration of the cellulose sulfate in the aqueous media.

The sulfating complex contains at least 1 mole of the N-dialkyl amide for each mole of sulfur trioxide and preferably 2 moles of the N-dialkyl amide are present for each mole of sulfur trioxide. In general, it is desirable to use a weight of SO₃-N-dialkyl amide complex which is at least two times the weight of the cellulose.

The cellulose sulfate salts employed in my invention are formed by neutralizing the free acid through reaction with a suitable base. The cellulose sulfate is a half-ester of sulfuric acid. Thus, one of the hydrogen ions originally present in the sulfuric acid is still free to react to give salts. As defined, the salts employed are water soluble and in aqueous solution give a pH of in excess of 6 to essentially neutral. Suitable salts, for example, are obtained by reaction of the acid with various bases to give alkali metal salts, such as sodium, lithium, potassium, ammonium, magnesium and the like, or with organic cations, especially short chain alkyl and alkylol

substituted ammonium, such as methylammonium, triethanolammonium, dimethyl-benzylammonium, and the like. Preferably, the salt is an alkali metal salt such as sodium or potassium.

The coating containing a suitable inert pigment dispersed in an aqueous solution of a salt of cellulose sulfate, as defined above, may be applied to the paper by means of any of the various conventional coating techniques such as the use of a roll, flexiblade, or air knife coater. In order to prevent curl, it may be desirable in some cases to apply the coating to the back side of the sheet also.

Following coating, the coated sheet is dried and is then treated with an aqueous solution of a soluble potassium salt. Various potassium salts may be employed such as potassium chloride, potassium sulfate, potassium carbonate, potassium bicarbonate, potassium citrate, potassium bromide, potassium pyrophosphate, potassium tartrate, potassium acetate, and the like. Preferably, potassium chloride is employed as the potassium salt. The concentration of the potassium ion in the aqueous treating solution is not critical so long as a sufficient amount of potassium ion is present to insolubilize the cellulose sulfate such that it is water resistant. When employing an aqueous solution of potassium chloride, I generally use approximately a 10% solution. Following treatment of the coated sheet with an aqueous solution containing a potassium salt, the treated sheet may then be water washed, if desired, and supercalendered or subjected to equivalent treatment to give the sheet the degree of gloss desired.

To further illustrate my invention, there are presented the following examples in which all parts and percentages are by weight unless otherwise illustrated.

Example I

In 41.3 grams of water were dispersed 96.7 grams of No. 2 kaolin coating clay. To this dispersion were added 242.7 grams of water and 19.3 grams of a relatively undegraded sodium cellulose sulfate having colloidal properties and a D.S. of about 2.2. The mixture was then agitated for a sufficient length of time to allow the sodium cellulose sulfate to dissolve. The total solids contained in the coating were 29% and the weight ratio of the sodium cellulose sulfate to the kaolin clay was about 20:100.

The coating was applied to 18 lb./ream litho rawstock using a No. 20 wire wrapped coating rod. The coated sheet was allowed to air dry after which it was passed through a 3% potassium chloride bath and then rinsed with distilled water. Drying was then effected by passing the sheet through a drum dryer at 180° F. with a 3 minute hold time. The sheet exhibited excellent web rub properties while at the same time it did not repel water. The coated surface accepted images in a satisfactory manner and was judged to be suitable for offset printing.

Example II

To 240 lbs. of water were added 10 lbs. of relatively undegraded sodium cellulose sulfate having colloidal properties and a D.S. of about 2.2. After the sodium cellulose sulfate had dissolved in the water, 50 lbs. of No. 2 kaolin coating clay were added thereto to form a dispersion. The resulting mixture was agitated until a constant minimum viscosity was obtained, which was 2700 cps. at 99° F. The viscosity of the mixture was determined with a Brookfield Model LVF Viscometer using a No. 4 spindle rotating at 60 r.p.m. The total solids contained in the coating mixture were 20% and the weight ratio of sodium cellulose sulfate to clay was 20:100.

After the coating mixture had attained a constant minimum viscosity, it was applied to a 20 lb./ream map rawstock by means of an air-knife coater. The coating speed was 500 feet per minute. Two coating passes were made on the top (printing) side and one coating pass was made

on the bottom side. The total coating pick-up was 6.5 lbs./ream with 6.0 lbs. on the top side and 0.5 lb. on the bottom side.

The printing surface was then treated with a 3% aqueous solution of potassium chloride using the air-knife coater. The coater speed was 200 feet per minute. Following treatment of the paper with potassium chloride, it was then dried and supercalendered in the normal manner to give the paper the desired gloss. The finished paper had the desired properties for use as an offset master paper.

In the foregoing examples, the paper employed was a high wet strength paper which had been previously sized in the normal manner. Although the sodium salt of an essentially undegraded cellulose sulfate was employed in these examples, satisfactory paper offset masters are obtained by employing any of the various water soluble salts of a relatively undegraded cellulose sulfate having colloidal properties and a D.S. of 1-3 as enumerated previously. Moreover, potassium salts, as defined previously, other than potassium chloride, may be employed in obtaining a satisfactory paper offset master.

It should be emphasized that the cellulose sulfate or salt thereof which I employ is quite unlike previously available cellulose sulfate. The material which I employ is relatively undegraded such that its salts, have colloidal properties. Previously obtainable cellulose sulfate had a degraded molecular structure due to the severity of the sulfation procedure. Such material does not have colloidal properties and is not suitable for preparing a paper offset master according to my invention.

In use, a greasy image is made on the paper offset master of my invention by any means such as typing, drawing or writing. The image is made with a suitable ink or pencil or equivalent means. The surface area which contains the image is grease receptive and will accept ink.

Following the placing of an image on the surface of the offset master, the surface is treated with an etching or fountain solution. The non-imaged areas of the offset master are both hydrophilic and water resistant. Thus, the non-imaged areas are wetted with the solution such that they will repel ink. Conversely, the image areas of the offset master are hydrophobic and are not wetted by the etching or fountain solution. These areas are grease receptive and will retain ink.

Many suitable etching solutions are available. As an example, a gum arabic solution with barium nitrate and water is available. The present invention is not limited to use of any particular fountain solution, many of which are known to the prior art.

After treatment of the offset master with fountain solution, the master is placed on an offset printing press. A thin film of an oil base ink is then applied to the master as, for example, by a roller. The ink is accepted by the imaged areas of the master which are oleophilic and is resisted by the non-imaged areas which are wetted with the etch or fountain solution. The ink image is used in offset printing in a well known manner by transfer to a drum and then to the paper.

Various image techniques can be employed in the use of the paper offset master of my invention. For example, the surface coating for the offset master can also contain ammonium bichromate to make it light sensitive. The coated master can then be placed in a printing frame in contact with a negative. On exposure to a strong light source for a suitable period of time, the plate is removed from the frame or other holding means and is separated from the negative. Following this, the developing ink is applied to the plate and the plate is developed out in a known manner. Any excess developing ink is removed and the plate is then preferably put under running water to remove the ink on all the areas except those areas which have been hardened and made insoluble by the light. The hardened and insolubilized areas are receptive to printing inks. Following this treatment, the plate is then

treated with an etch or fountain solution in the manner described previously, then a thin film of ink is laid down on the plate, and it is used in the known manner in an offset printing press.

Also, the paper offset master of my invention may be made photosensitive. To do this, silver salts, such as silver bromide or silver chloride or silver iodide or any combination thereof, are added to the surface coating along with the cellulose sulfate salt, water, and pigment in the amount described previously. Following drying of the coating, etc., the paper offset master is ready for exposure, developing and fixing operations and for further use. In use, the plate, together with the negative is subjected to a light of suitable intensity. After sensitization, the plate may be either used for contact printing or enlargement and after a suitable exposure the usual photographic steps of developing and fixing are carried out and the exposed silver salts are reduced to metallic silver.

The reduced metallic silver now present in the developed and fixed plate is not grease receptive and will not accept greasy inks. Thus, the reduced metallic silver may then be converted into a chromate salt by the use of a suitable bleaching agent. After the plate has been treated with the bleach, the image is grease receptive. After the bleaching operation, the plate is treated with the developing ink and on completion of that treatment is ready for use as an offset printing plate.

As shown by the foregoing description, my invention is a broad one having a wide variety of applications. Although I have described my invention by reference to specific examples, I do not intend my invention to be limited except by the lawful scope of the appended claims.

I claim:

1. A process for forming a direct image paper offset master, said process comprising coating a high wet strength paper with an aqueous coating composition containing an inert pigment and a water soluble salt of a colloidal cellulose sulfate having a D.S. of 1 to 3 and having a viscosity at a 1% concentration in an aqueous media in excess of 20 cps. as measured by a Brookfield Synchro Electric Viscometer, Model LVF, at 60 r.p.m. and a temperature of 25° C., said salt being characterized as one which in aqueous solution gives a pH from in excess of 6 to about 7, drying said coated sheet and treating the sheet with an aqueous solution of a soluble potassium salt in a sufficient amount to insolubilize the said cellulose sulfate salt such that it is water resistant.

2. The process of claim 1 wherein said cellulose sulfate salt is present in said coating composition at a weight ratio from about 10:1 to about 3.33:1 with respect to said pigment.

3. The method of claim 2 wherein said cellulose sulfate salt is present in said coating composition at a weight ratio from about 5:1 to about 4:1 with respect to said pigment.

4. The process of claim 2 wherein said coating composition contains from about 60 to about 85% by weight of water.

5. The process of claim 3 wherein said coating composition contains from about 70 to about 75% by weight of water.

6. The process of claim 3 wherein said direct image paper offset master is supercalendered to give it the de-

sired degree of gloss following treatment with said soluble potassium salt.

7. The process of claim 1 wherein said water soluble cellulose sulfate salt is an alkali metal salt.

8. The process of claim 7 wherein said water soluble cellulose sulfate salt is a sodium salt.

9. The process of claim 7 wherein said water soluble cellulose sulfate salt is a potassium salt.

10. The process of claim 1 wherein said soluble potassium salt is potassium chloride.

11. The process of claim 10 wherein said potassium chloride salt is present in said aqueous solution at a concentration of about 10% by weight.

12. The process of claim 1 wherein said direct image paper offset master is supercalendered to give it the desired degree of gloss following treatment with said soluble potassium salt.

13. The process of claim 1 wherein said colloidal cellulose sulfate has a D.S. in excess of 2.

14. A direct image paper offset master prepared according to the method of claim 6.

15. A direct image paper offset master prepared according to the method of claim 12.

16. A coating composition comprising an inert pigment, a water soluble salt of a colloidal cellulose sulfate having a degree of substitution in the range of 1 to 3 which forms gels in aqueous solution on the addition thereto of potassium ions and said salt having a viscosity at a 1% concentration in an aqueous media in excess of 20 cps. as measured by a Brookfield Synchro Electric Viscometer, Model LVF, at 60 r.p.m. and a temperature of 25° C., said cellulose sulfate salt being characterized as producing a pH in aqueous solution ranging from in excess of 6 to about 7, with the weight ratio of said cellulose sulfate salt to said pigment ranging from about 10:1 to about 3.33:1, and from about 60 to about 85% by weight of water.

17. The coating composition of claim 16 wherein the weight ratio of said cellulose sulfate salt to said inert pigment ranges from about 5:1 to about 4:1, and the water content ranges from about 70 to about 75% by weight.

18. The composition of claim 16 wherein said water soluble cellulose sulfate salt is an alkali metal salt.

19. The composition of claim 18 wherein said cellulose sulfate salt is a sodium salt.

20. The composition of claim 18 wherein said cellulose sulfate salt is a potassium salt.

21. The coating composition of claim 16 wherein said colloidal cellulose sulfate has a D.S. in excess of 2.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

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It is certified that error appears in the above identified patent and that said Letters Patent are hereby corrected as shown below:

Column 5, lines 49 and 50, 53 and 54, and column 6, lines 34 and 35, "cellulose sulfate salt", each occurrence, should read -- pigment --; same column 5, lines 52 and 56, and same column 6, line 35, "pigment", each occurrence, should read -- cellulose sulfate salt --; same column 6, line 39, "cellulose sulfate salt" should read -- inert pigment --; lines 39 and 40, "inert pigment" should read -- cellulose sulfate salt --.

Signed and sealed this 2nd day of September 1969.

(SEAL)

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Commissioner of Patents