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2,940,890

TREATMENT OF CELLULOSIC PULPS

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No Drawing. Filed June 25, 1956, Ser. No. 593,326

4 Claims. (Cl. 162—111)

The present invention in general relates to the treatment of cellulosic pulps which have not been utilizable for certain purposes so as to make them available for use in manufacture of various cellulosic products. In particular, this invention relates to a manner of treating certain pulps which ordinarily produce hard and brittle tissues so that they may be manufactured into a high grade, soft facial tissue.

In the past, most high quality cellulosic products as, for example, facial tissue, have been made from sulphite pulp from wood grown in the north central or northeastern sections of the United States, or from wood which is grown in the central and eastern sections of Canada. Sulphite pulp from wood produced in the areas mentioned produces a strong, soft cellulosic fiber which may be readily utilized for the preparation of high quality creped sheets for use as facial tissue or the like. Tissues made from such pulp are soft and strong and have a very desirable texture for use on skin areas.

With the increase in the use of cellulosic products it has been necessary to attempt to produce products including facial tissues from pulp made from wood grown in other areas. However, attempts to utilize these pulps except as a fraction of the entire pulp in the furnish, have resulted in harsh, brittle sheets which do not produce facial tissues of high quality and even the production of the harsh sheets is difficult because the heat applied to the sheet on the dryer in the papermaking machines causes it to stick to the dryer surfaces. This sticking results in tears on the sheet which interfere with the efficient operation of the machine.

Commercially available pulps which cause these difficulties and which are unsatisfactory for tissue products, include all kraft pulps and pulps made from the commercially used pulp woods grown on the west coast of the United States which are pulped by the sulphite process. For example, the limited utility of kraft pulps substantially reduces the use of Southern Pine pulps for facial tissues since almost all of that wood is pulped by the kraft process. These pulps result in harsh, rough tissue material which has a marked brittleness and a serious tendency to stick to the surfaces of the dryer and to tear at the creping doctor. These latter difficulties result in inefficiencies on the paper-making machine and in the converting operation, and greatly increases the amount of broke which must be reworked. Another difficulty which manifests itself when these pulps are employed is the lack of "life" in the sheet from the papermaking machine, i.e., the sheet does not stretch readily and is relatively inelastic, which prevents the obtaining of the proper stretch in the sheet in the rewinding operation. This, too, contributes to the production of a harsh sheet and to decreased yardage for a given weight of pulp.

Accordingly, the principal object of this invention is to modify kraft pulps and west coast sulphite pulps so that they are useful in making a high grade product such as a facial tissue or the like and to so condition the pulps that the difficulties on the papermaking machine are ob-

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viated. Other objects and advantages of the invention will become known by reference to the following description of various preferred embodiments of the invention.

The reasons for the difficulties with kraft pulp and with west coast sulphite pulps are not wholly understood. Theories have been advanced involving the chemical constituents in the pulp, and the warmer temperatures in the southern and western areas which result in the rapid growth patterns of the trees which result in excessive amounts of summer wood and a coarse fiber structure. However, none of the theories or explanations of the reasons for the poor results which are obtained when either kraft pulps or west coast sulphite pulps are employed has resulted in a substantial improvement in products made from the pulp.

I have discovered that these kraft and sulphite pulps can be so conditioned as to obviate the prior difficulties and make them usable for the manufacture of high quality facial tissue by supplying the pulp to the papermaking machine in a furnish which contains a small percentage of a fatty acid having between 6 and 18 carbon atoms and which is maintained at a pH of less than about 6.5. The fatty acids may be added in various ways and at different points in the system. Preferably, the fatty acid is added to the pulp at any point in the papermaking system where the pulp will remain in a moist or wet condition, i.e., in the form of a pulp or slurry containing more than about 40 percent of water, until the time that the web is finally formed. Most desirably, however, the addition is made to the system at a point where the pulp will remain in slurry form, i.e., dispersed in water, until the web is formed. However, in the case of fatty acids which are liquid at the temperature of repulping, e.g., oleic acid, the acid may be added to the pulp after bleaching and washing in the pulp mill. The pulp may then be dried, shipped, and again dispersed in water without materially effecting the effectiveness of the conditioning.

It has been found that the addition of the fatty acids in an amount of less than .75 percent based on the weight of oven dry pulp, produces marked increases in softness of the pulp, reduces brittleness and minimizes sticking to the heated surfaces of the dryer. In addition, it is found that the addition of the fatty acid provides a more elastic and stretchable tissue and it has been found that the speed of the papermaking machine may be increased materially because the formed sheet for some unknown reason contains less moisture when it reaches the dryer than a sheet which has not been so conditioned.

The fatty acid may be added to the pulp in any manner which will secure an efficient dispersion of the acid in the pulp. The preferred method of dispersing the fatty acid into the pulp is to first transform the fatty acid into a soap which is then dispersed in a pulp slurry or in the final furnish. When this method of dispersion is employed the slurry or furnish is either acidified or is held at an acid level which will be effective to break the soap down to produce the free acid.

Sulphonated fatty acids from the group previously defined may be used to attain the advantages of the invention. These compounds may be added to the pulp slurry or furnish under acidic conditions and are readily dispersible in the pulp suspension to provide the necessary fatty acid content.

Another method of dispersing the fatty acid involves dispersing the acid in a volatilizable solvent for the acid such as alcohol or ether and spraying it onto a moist pulp mat or into the pulp in water suspension while it is being vigorously agitated, the fatty acid then becoming incorporated with the pulp and attached to the cellulosic particles therein, after which the solvent evaporates.

As has been pointed out, the fatty acids which contain from 6 to 18 carbon atoms will condition the pulp so as

to accomplish the objects of this invention. Of course, certain of the acids can not be used in pulp to be used in a facial tissue type of product because of the inherently odorous nature of the compound as, for example, n-caproic acid ($C_6H_{11}COOH$). However, these odorous compounds may be employed to enhance the properties of the sheet and to increase the efficiency of the papermaking operation if the end product is to be used for a purpose where odor is not a problem or where it can be masked by a suitable masking agent.

It has been found too that the degree of unsaturation of the acid is also a factor in papermaking machine operation since highly unsaturated fatty acids tend to polymerize when subjected to heat on the dryer and thereby produce a film or varnish on the heated sections of the drying apparatus which are exposed to the compound. As such films build up they decrease the heat transfer efficiency of the dryer and finally render it inoperable. Thus for practical operation on a papermaking machine the degree of unsaturation desirably should not exceed one double bond. For example, oleic acid ($C_{17}H_{33}COOH$) provides excellent results and does not result in film build up on the drying equipment. However, acids with greater degrees of unsaturation such as linoleic acid ($C_{17}H_{31}COOH$) and linolenic acid ($C_{17}H_{29}COOH$) are not satisfactory because of their tendencies to polymerize.

It is sometimes convenient to employ mixtures of these fatty acids as are distributed by the various suppliers and which include both saturated and unsaturated compounds. When these mixtures are employed the tendency to varnish film formation should be evaluated to determine whether or not it presents a problem with the temperatures being employed and also the odor characteristics of the mixture should be considered in connection with the end use contemplated for the product.

Specific Example I

A sodium soap of oleic acid was made by mixing in 4000 parts by weight of water, 100 parts by weight of oleic acid and 20 parts by weight of sodium hydroxide. To this solution there was added 10 parts by weight of a nonionic dispersing agent (a polyoxyethylene ether of an alkylphenol) sold under the trade name Igepal CO-630 by the Antara Chemical Company. The dispersing agent was added to the mixture to insure that the free fatty acid would be deposited in finely dispersed form on the cellulosic fibers. The dispersing agent also minimizes the interaction of oleic acid with the calcium ions which are present in the white water system, which tends to form an insoluble calcium soap.

This oleic acid soap solution was fed into the feed conduit to the fan pump which pumped the furnish to the inlet of the papermaking machine. The machine was employing a furnish which included 100 percent of west coast pulp in the manufacture of creped tissue sheets. The pulp included 35 percent west coast sulphite pulp and 65 percent west coast kraft pulp. The pulp in the furnish had, previous to the addition of the above solution, caused considerable difficulty in that it adhered to the surface of the Yankee dryer and the sheet produced was extremely harsh, it did not crepe properly, nor did it stretch properly as it was rewound.

The above solution of oleic acid and caustic, i.e., the sodium soap of oleic acid, was fed into the system at a rate such that .25 pound of oleic acid as the sodium soap, was metered into the pump for every 100 pounds of oven dry fiber which was being produced by the machine. As the soap solution was added, the white water system of the machine was maintained at a pH of from 6.0 to 6.5 by the addition of sulphuric acid to effect the conversion of the sodium soap back to the free oleic acid.

Upon the addition of oleic acid soap the sheet so adhered to the dryer that it creped properly and the re-

sulting product exhibited the same stretch and softness as are observed with high quality facial tissue sheets.

Specific Example II

The sodium soap solution of oleic acid which was described in Example I above was added to the pulp in the re-pulper of a papermaking system which was employing as its pulp 35 percent west coast sulphite and 65 percent west coast kraft pulps. This solution, which included 100 parts by weight of oleic acid, 20 parts by weight of sodium hydroxide, 4000 parts by weight of water, and 10 parts by weight of a dispersing agent, was added to the pulp which had been first acidified to a pH of 5 with hydrochloric acid. Enough of the solution was added to the pulp to provide .4 percent oleic acid based upon the oven dry weight of pulp in the re-pulper. In the re-pulper the solution was thoroughly mixed with the pulp and water slurry and the pH in the re-pulper rose to approximately 6.0 after the addition of the solution. After the oleic acid solution was thoroughly dispersed, the furnish was refined in the usual manner and supplied to the inlet of the papermaking machine.

It was found that this pulp when made into creped tissue exhibited the proper degree of adhesion to the dryer and produced a soft facial tissue of the highest quality. This tissue showed the normal stretch and elasticity as it was rewound.

The employment of the oleic acid enabled the speed of the machine to be increased about 5½ percent.

Specific Example III

A sodium soap solution of oleic acid which included 100 parts by weight of oleic acid, 20 parts by weight of sodium hydroxide, and 4000 parts by weight of water as described in Example I above was added to the pulp slurry in a pulp mill prior to drying. The pulp was a 100 percent kraft pulp made from spruce and jack pine. Enough of the solution was added to the pulp to provide .4 percent oleic acid based upon the oven dry weight of pulp and the solution was thoroughly mixed in the pulp and water slurry. To this mixture there was added an excess of calcium chloride to transform all of the sodium oleate soap into a calcium soap and the slurry was again agitated. Finally, the pulp slurry containing the calcium soap was acidified with hydrochloric acid to a pH of 5.0 to provide free oleic acid.

The resulting slurry was then dried to produce a pulp containing about 80 percent fiber on an air dried basis, after which it was shipped to a paper mill. At the mill the pulp was diluted with water and refined to form a slurry and pumped to the inlet of a papermaking machine.

It was found that this pulp when made into creped tissue did not stick excessively to the dryer and produced a soft facial tissue of the highest quality. This tissue showed the normal stretch and elasticity as it was rewound.

The employment of the oleic acid enabled the speed of the machine to be increased from between 5 and 10 percent over a furnish which involved the use of 65 percent Canadian sulphite pulp and 35 percent of the untreated kraft pulp above referred to.

Specific Example IV

A solution of oleic acid in ethyl alcohol was sprayed onto a southern pine kraft pulp having a consistency of about 40 percent. Enough of the alcohol solution was added to provide .4 percent oleic acid based upon the weight of oven dry pulp. This pulp was further diluted with water, refined, and made into a hand sheet. The hand sheet was tested for dryer sticking in the laboratory and exhibited satisfactory properties while a similar hand sheet made without the oleic acid could not satisfactorily be removed from the test dryer surface.

Specific Example V

An emulsion of stearic acid and water comprising 100

parts by weight of stearic acid and 4000 parts by weight of water was made by adding enough sodium hydroxide to permit emulsification under agitation. This emulsion was added to a slurry of southern pine kraft pulp in water in an amount such that there was 0.3 percent by weight of stearic acid based upon the weight of oven dry pulp. The pH was adjusted to between 6 and 6.5 by the addition of hydrochloric acid and a hand sheet was made from the pulp slurry. The hand sheet was tested for dryer sticking in the laboratory and exhibited satisfactory properties while a similar hand sheet made from the untreated pulp could not satisfactorily be separated from the dryer surface.

Specific Example VI

Sulphonated oleic acid was added to a slurry of southern pine kraft pulp in water in an amount such that there was 0.75 percent by weight of oleic acid based upon the weight of oven dry pulp. The pH was adjusted to about 4.0 by the addition of hydrochloric acid. A hand sheet was made from the pulp slurry. The hand sheet was tested for dryer sticking in the laboratory and exhibited satisfactory properties while a similar hand sheet made from the untreated pulp could not satisfactorily be separated from the dryer surface.

My experiments have shown that the other fatty acids which have not more than one unsaturated bond and which include a carbon chain of from 6 to 18 carbon atoms may be successfully substituted for the acids mentioned above, except that in a process of the type described in Example III where the pulp is dried, acids which are liquids at the temperature of repulping should be employed. Repulping temperatures generally fall within the range of 60 to 90° F.

Of course, if a product is being manufactured which has special use such as facial tissue, the properties of the fatty acids should be taken into account in selecting the acids for, as has been pointed out, caproic acid and several of the other acids have objectionable odors which may not be dissipated before the product is used. The level of the fatty acid, as has been pointed out, is desirably below about 0.75 percent by weight, based upon the weight of oven dry pulp. Commercial ranges ordinarily are between about 0.1 and 0.5 percent, with the preferred range being between about 0.20 and 0.40 percent by weight.

It should be borne in mind regardless of which acid is used that the pH in the papermaking system should be maintained at a point below 6.5, above which point the fatty acids tend to form insoluble soaps with any calcium or magnesium which may be present in the system, such insoluble soaps causing a great deal of difficulty in cleaning the equipment and impairing its efficiency. In order to insure that the insoluble soaps do not cause difficulty, it has been found desirable to operate at a pH of 6.0 or below so as to provide a greater margin of safety. Care should also be taken to maintain all parts of the machine and system which contact the fatty acid content pulp and whitewaters at

a pH below 6.5, and preferably below 6.0. This will obviate plugging or clogging the wire or felts with insoluble precipitates. In acidifying the system it has been found that the mineral acids or sulfur dioxide may be employed with equivalent results.

While various of the features of the invention have been described in connection with facial tissue quality sheets, the invention has equal applicability to other cellulosic products made from kraft pulps and west coast sulphite pulps and minimizes the problems which occur as a result of the relatively harsh brittle quality of such products.

The exact mechanism which causes the change in the character of these cellulosic products is not entirely clear but it would appear as though the fatty acid in some way becomes attached to the cellulosic fibers so as to enhance water release and drying characteristics and to alter in some way the fiber bonds or even the characteristics of the cellulosic fibers. This is borne out by the fact that the fatty acid adheres to the cellulosic fibers and is not appreciably reduced in concentration by high velocity pressure forming inlets or the refining of the pulp.

Various features of the invention are set forth in the appended claims.

I claim:

1. A process for utilizing wood pulp selected from the group consisting of kraft pulp, west coast sulphite pulp and mixtures thereof in the manufacture of a soft, pliable, dry creped cellulosic tissue product which consists in the steps of dispersing said pulp in water, introducing a small amount of a selected fatty acid into the pulp dispersion, said amount of fatty acid being between about 0.1 and 0.75 percent by weight of the oven dry pulp, said fatty acid having not more than one unsaturated bond and from 16 to 18 carbon atoms, maintaining the pulp dispersion at a pH of less than about 6.5 with a mineral acid, forming a continuous web from said dispersion, drying said web on a Yankee dryer, and continuously creping said web from said dryer.

2. The process of claim 1 wherein said fatty acid is oleic acid.

3. The process of claim 1 wherein said fatty acid is introduced into said pulp dispersion as a fatty acid soap solution.

4. The process of claim 3 wherein said fatty acid soap solution is the sodium soap of oleic acid in aqueous solution.

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