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METHODS OF DEWAXING PAPER

Henry B. Hope, Mount Vernon, N. Y., assignor to R. H. Comey Company, Inc., Brooklyn, N. Y., a corporation of New York

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This invention relates to the reclaiming of paper and other cellulosic products, and more particularly to methods for recovering both the cellulosic and the waxy constituents of waxed or paraffin paper waste.

The general object of the invention is to provide novel and improved processes for the treatment of waxed paper waste for the economical recovery of the wax and the paper therefrom, both in condition for re-use. The invention has particular application to the treatment of waxed paper of either the sulfite or sulfate types, whereby the recovery of the valuable high-grade paper stock in a satisfactory hard and sufficiently undeteriorated condition may be effected.

Previous attempts to recover profitable percentages of high-grade paper fiber and of the waxy constituents of such waste paper have not been successful. Various processes involving treatment with alkaline agents and organic solvents have failed to produce high yields of either paper or wax, either through deterioration of the paper fibers or to penetration of the wax into the paper stock. Although it is possible that a somewhat purer grade of wax might ultimately be obtained by the use of such solvents, the reduction in yield and the poor grade of fiber recovery, as well as the fire hazards, excessive costs, and difficult operational problems, render such processes commercially inpracticable. It has also been found that the use of emulsifiers of some types leaves undesirable foreign materials in the recovered product.

It is therefore a further object of the present invention to provide processes of the class described by which a high yield of wax and high-grade paper fiber may be obtained, by which complete removal of the wax from the paper may be effected, and by which the cellulosic fiber yield is of a strong, hard, light colored nature.

In its preferred embodiment, the invention contemplates the provision of a recovery process which, broadly expressed, comprises treating waste wax paper in a heated aqueous acid solution of a detergent of the alkali-metal higher-alkyl sulfonate type, either with or without an aryl radical; it being understood that in this context the ammonium radical is considered the equivalent of an alkali metal. These detergents are generally marketed as white or light-colored flaky solid materials, neutral in reaction and highly resistant to acids and alkalies and to oxidation, readily soluble in soft water, hard water, and in solutions of acids or alkalies. As examples of these agents, there may be mentioned the commercial Nacconol NR and MP-189. I am advised that the former product contains as its active ingredients approximately 40% of sodium alkyl benzene sulfonate, the alkyl radical containing an average of twelve carbon atoms. The material designated MP-189 is a

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commercial product containing approximately 30% to about 40% sodium alkyl (approximately C_{16} to C_{17}) sulfonate.

This bath serves to melt and coagulate the wax and initiate its separation from the paper stock, and at the same time the paper fibers are thoroughly wetted. The coagulated and melted wax may be skimmed or drawn off the surface of the bath.

Following the first detergent bath, the material is immersed for a brief period in a heated bath comprising an aqueous solution of sodium chlorite ($NaClO_2$) or other chlorine containing or gas producing bleaching agent, for the dual purpose of evolving gas at the surface of the cellulose material beneath the remaining wax in order to further loosen the wax constituent, and to bleach the product and thus improve its appearance. Sulfur dioxide and hydrogen peroxide bleaching agents may also be employed in substitution for the chlorine generating bleaches.

After the treatment in the bleaching bath, the material is immersed in a second acid-detergent bath to remove the balance of the wax and coagulate it so that it may be skimmed off. After draining from this further detergent bath, the material is preferably immersed in hot water, preferably containing a neutralizing agent for a period and then finally drained and dried at about 105° C.

By pursuing the complete process comprised in and forming a part of the present invention, substantially perfect removal of the wax is attained and a very high-grade, hard, sufficiently undeteriorated, light colored reclaimed paper product is recovered. However, by resorting to certain changes within the broad scope of the invention, commercially acceptable but lower grade products for various purposes may be produced. For example by omitting the sodium chlorite or other bleaching or gassing bath, a somewhat dark colored product results which is less pleasing in appearance and which contains some unrecovered wax, say about 5% by weight, or approximately 20% of the original wax content.

A reduction in the strength of the wetting-detergent agent in either or both of the acidulated baths will yield a commercially acceptable product which is not completely wax free. It is also to be understood that the preferred acids to be used in combination with the wetting-detergent agents are hydrochloric, sulfuric, and nitric acids. Hydrochloric and sulfuric acids are much to be preferred, and phosphoric, acetic, and oxalic acids, although workable in some degree in cruder recovery processes, are not as satisfactory as the preferred acids.

It has been found that the acid-wetting-agent baths should be operated at temperatures from about 90° C. to about 99° C., although an actual

boiling of the solution has resulted most satisfactorily, within the range of time limits described herein. The wax starts to come off appreciably at about 80° C., and it is to be understood that by varying the degree of agitation, altering the concentration of the solution, and varying the time of treatment, various temperatures can be employed from 80° C. to 100° C. with somewhat varying effects on the paper fibers.

The apparatus for carrying out the present process is not particularly a part of the present invention and may be varied as desired. The various baths may be contained in circulatory tanks provided with agitators and susceptible of being readily filled and drained, or the scrap or waste product may be contained in mesh or perforated cages capable of being immersed and withdrawn from the separate baths.

The process is designed to effect the recovery of waste wax paper of any type, among which may be mentioned paper milk containers, paper food containers, Lily cups, soda straws, or the like. After final draining and when prepared for shipment, the water content of the processed paper is approximately 50%.

Some of the wax remains in solution, especially in the case of the first acid-detergent bath, and this wax, as desired, may be precipitated by cationic action. However, it may not be commercially economical to pursue this step.

There follows a series of specific examples of the pursuit of the present invention, and it is to be understood that these same specific processes may be employed with the substitution of any of the wetting-detergent agents stated to be satisfactory, as well as variation in the acids used, within the range of those which will give adequate but somewhat inferior results. Also, in the use of acids other than hydrochloric and sulfuric, it is sometimes advisable to vary the exemplary processes described by effecting a subsequent neutralizing step.

Example I

Fifteen kilograms of mechanically cut waxed paper containers were added to a first treating bath containing 1.30 kilograms of Nacconol NR and 3 liters of 9% sulfuric acid in water to make 180 liters, at 95° C. The bath was hand stirred and maintained at from 96° C. to 99° C. by direct steam for one hour during which time the wax coming to the surface was skimmed off, a screen being applied to hold the paper down in the bath while the wax was ladled from the surface.

After one hour, the bath was drained off and a new bath introduced which comprised 35 grams of sodium chlorite in water to make 100 liters. This bath was kept at 70° C. with stirring for fifteen minutes, and the further separated wax being skimmed off during this time.

This bath was drained off and a new bath introduced, at 90° C., and consisting of 500 grams of Nacconol NR and 2 liters of 9% sulfuric acid, in water to make 100 liters. This third bath was kept at from 95° C. to 99° C. for one hour, with stirring and skimming of the wax as previously described.

After one hour, the bath was run off and plain water at 70° C. was added, this rinsing bath being stirred for five minutes and then run off.

Example II

A batch of 480 kilograms of Lily cups cut to about one-half to three inch sizes was added to a bath comprising 3500 liters of water at 90° C., 70 kilograms of Nacconol NR, and 176 liters of 9% sulfuric acid. This being a rather large bath and difficult to thoroughly agitate, the time of treatment was extended to five hours at from 95° C. to 96° C. The wax developed was skimmed off and at the end of five hours the batch which was contained in a basket or cage was lifted out of the bath, drained for fifteen minutes, and then introduced into a second bath comprising 3500 liters of water at 70° C. and 3.5 kilograms of sodium chlorite. The bath was agitated, the wax skimmed, and after ten minutes the batch was removed and drained.

The third bath comprises 3500 liters of water at 90° C., 35 kilograms of Nacconol NR, and 105 liters of 9% sulfuric acid. The bath was kept at from 95° C. to 99° C. for one hour with agitation and the remaining wax was skimmed off. The material was drained and then rinsed in 3500 liters of water for twenty minutes, then removed and treated again with a bath of water into which was dissolved two kilograms of sodium bisulfite at 70° C. The material was agitated for one-half hour, no wax appearing. Then the recovered product was removed and drained.

Example III

A batch of 105 grams of cut waxed milk containers was stirred in a bath comprising 1 liter of water at 90° C., 7 grams of Du Pont MP–189, and 24 cubic centimeters of 9% sulfuric acid. The bath was kept at from 95° C. to 99° C. and the wax skimmed off. After one hour the bath was drained and a second bath comprising 0.3 of a gram of sodium chlorite in 1 liter of water at 70° C. After stirring and skimming the wax for ten minutes the bath was drained and a third bath introduced comprising 1 liter of water at 90° C., 5 grams Du Pont MP–189, and 19 cubic centimeters of 9% sulfuric acid. The bath was stirred for one hour at 95° C. to 99° C., the wax being skimmed. The bath was then drained and the product removed for drying.

Example IV

A batch of 45 kilograms of cut waxed milk containers was introduced into a first bath comprising 540 liters of water at 90° C., 4 kilograms of Nacconol NR, and 9 liters of 9% sulfuric acid. The treatment was continued for one hour at 95° C. to 99° C. The second bath comprised 300 liters of water at 70° C. and 105 grams of sodium chlorite. After stirring and skimming the wax for fifteen minutes at 70° C. the bath was drained and then plain water was added at 90° C., and kept at 95° C. to 99° C. while stirring the batch and skimming the wax. After one-half hour the bath was drained and the product removed.

Example V

A batch of 270 kilograms of waxed soda straws was treated in a bath comprising 3500 liters of water at 90° C., 17.5 kilograms of Nacconol NR, and 70 liters of 9% sulfuric acid. After agitating, and skimming the wax, for two hours at 95° C. to 99° C. the bath was drained and the paper removed and treated in a second bath for ten minutes at 70° C., this bath comprising 5 kilograms of sodium bisulfite in 3500 liters of water. The third bath comprised 3500 liters of water at 90° C., 17.5 kilograms Nacconol NR, and 80 liters of 9% sulfuric acid. After stirring and skimming at 95° C. to 99° C. for one

hour, the bath was drained and a final rinsing effected in 3500 liters of water introduced at 90° C., the agitation during rinsing lasting for ten minutes at 95° C. to 99° C.

Example VI

A lot of 100 grams of waxed milk containers ripped and broken to about one-half to three inch sizes to avoid trapping any melted wax, was treated in a first bath comprising one liter of a 1% solution of Nacconol NR containing 7 milliliters of hydrochloric acid. This bath was raised to the boiling point before the cage containing the paper material was introduced. The bath was boiled for one hour, the wax being skimmed off the surface, the bath occasionally being surged to promote the action.

The cage was raised and allowed to drain and then immersed in a hot 0.2% sodium chlorite solution for about five minutes, whereupon the cage was again raised and allowed to drain. Then the material was immersed in a third bath comprising a liter of 1% Nacconol NR solution containing 3.5 milliliters of concentrated hydrochloric acid. The bath was boiled for one hour and the small amount of remaining wax skimmed off the surface. The cage was raised and the material allowed to drain and then immersed once in pure boiling water for about five minutes, and then drained and dried at about 150° C. The removal of wax was 100% complete.

Example VII

This run was exactly the same as Example VI above with the exception that the acid used was sulfuric acid and was employed in the amount of 25 cubic centimeters of 9% sulfuric acid in the bath of 1 liter.

Example VIII

One hundred grams of wax paper were agitated for one hour at 98° C. in a bath comprising 1 liter of water and 0.7% Nacconol NR together with dilute sulfuric acid to a pH number of pH 1.3. The liberated wax was removed from the bath during the treatment and the bath was drained. Then the material was treated in a second bath comprising 1 liter of water with 0.1% sodium chlorite which bath was poured on the material at 9.0 pH. The bath was stirred for ten minutes at 65° C., and additional wax removed.

After draining the material was agitated for one-half hour at 98° C. in a bath comprising 1 liter of water with 0.5% Nacconol NR and dilute sulfuric acid to about pH 1.3. Further wax was removed and the bath drained. The material was then agitated with plain water for ten minutes at 65° C., drained, and then agitated with plain water at 65° C. to which sodium hydroxide was added to a pH of 6.0.

Example IX

The treatment of Example VIII was repeated in connection with a batch of waxed paper, the only change being that the wash water bath was eliminated, the final treatment being the neutralization by the addition of sodium hydroxide.

In all of the examples given, a generous or repeated rinsing or washing with plain water will remove the acid, but it is within the purview of the invention to expedite the neutralization by addition of sodium hydroxide as set forth in Example VIII.

Summarizing the scope of the invention as set forth herein, it may be stated that the ratio of amount of stock treated to the volume of the baths employed may vary rather widely but it is suggested that for each kilogram of stock there be employed from about 6 to about 14 liters of bath. As to the first acid-detergent bath the amount of wetting-detergent-scouring compound used may vary from about 0.4% to about 1.9% and the amount of acid used is that sufficient to establish a pH of 2 or less. The time of treatment in the first bath may vary from about fifteen minutes to about five hours, depending somewhat on the concentration of the solutions, the amount of material treated, and the degree of agitation possible. Extreme agitation will considerably shorten the time, say down to about fifteen minutes, under the best conditions of temperature and concentration. The temperatures of treatment may vary from about 70° C. to about 100° C. The bleaching and gassing bath which is ordinarily the second treating bath may contain only a trace of bleaching and gassing compound, that is, only sufficient to give gassing at the surface of the paper. The time of treatment in this bath may run from a few minutes to about fifteen minutes, and the operating temperature may be from approximately 70° C. up to and including the boiling point. The ranges of characteristics of the third bath, if it is used, may be as follows: the amount of wetting-detergent agent used may vary from about 0.4% to about 1.0% and the acid may be such as will give a pH of 2 or less. As already indicated, a final bath may be provided of either plain water for rinsing or water containing a neutralizing agent such as NaOH, or a further bleaching treatment may be applied.

Various changes and modifications may be made in the embodiments described herein without departing from the scope of the invention as defined by the following claims.

Having thus described the invention, what is claimed as new and desired to be secured by Letters Patent is:

1. The process for reclaiming wax-paper products which comprises, in combination, digesting a quantity of such products in a first bath comprising an aqueous solution containing from about 0.4% to about 1.9% of an organic sulfonated wetting-detergent-scouring agent, selected from the group consisting of alkali-metal alkyl sulfonates and alkali-metal alkyl aryl sulfonates, and sufficient strong acid to yield a pH number of from approximately pH 1.3 to about pH 2, at a temperature of from about 70° C. to about 100° C., for from about fifteen minutes to about five hours, whereby the waxy constituent is for the most part separated from the product, and rises to the surface of the bath; skimming the wax from the surface; draining the product from the first bath, and treating it in a second bath comprising an aqueous solution containing from about 0.03% to about 0.2% of a gas evolving bleaching agent at approximately 70° C., for from about ten minutes to about fifteen minutes, whereby remanent wax is dislodged from the product and rises to the surface bath; skimming off the wax; and finally rinsing the wax-free paper product with water.

2. The process for reclaiming wax-paper products which comprises, in combination, digesting a quantity of such product in a first bath comprising an aqueous solution containing from about 0.4% to about 1.9% of an organic sulfo-

nated wetting-detergent-scouring agent, selected from the group consisting of alkali-metal alkyl sulfonates and alkali-metal alkyl aryl sulfonates, and sufficient strong inorganic acid to yield a pH number of from approximately pH 1.3 to about pH 2, at a temperature of from about 70° C. to about 100° C., for from about fifteen minutes to about five hours, whereby the waxy constituent is for the most part separated from the product, and rises to the surface of the bath; skimming the wax from the surface; draining the product from the first bath, and treating it in a second bath comprising an aqueous solution containing from about 0.03% to about 0.2% of a gas evolving bleaching agent at approximately 70° C., for from about ten minutes to about fifteen minutes, whereby remanent wax is dislodged from the product and rises to the surface bath; skimming off the wax; draining the product from the second bath; and treating it in a third bath comprising an aqueous solution containing from about 0.4% to about 1.0% of an organic sulfonated wetting-detergent-scouring agent equivalent to that used in the first treating bath and strong acid to maintain a pH number of from approximately pH 1.3 to about pH 2, at a temperature of from about 70° C. to about 100° C., for approximately one hour; and finally rinsing the wax-free paper product with water.

3. The process for reclaiming wax-paper products which comprises, in combination, stirring a quantity of such products in a first bath comprising an aqueous solution containing from about 0.4% to about 1.9% of an organic sulfonated wetting-detergent-scouring agent, selected from the group consisting of alkali-metal alkyl sulfonates and alkali-metal alkyl aryl sulfonates, and strong inorganic acid to yield a pH number of from about pH 1.3 to about pH 2, at a temperature of from about 70° C. to about 100° C., for from about fifteen minutes to about five hours, whereby the waxy constituent is for the most part separated from the product, and rises to the surface of the bath; skimming the wax from the surface; draining the product from the first bath, and stirring it in a second bath comprising an aqueous solution containing from about 0.03% to about 0.2% of a gas evolving bleaching agent at approximately 70° C., for from about ten minutes to about fifteen minutes, whereby remanent wax is dislodged from the product and rises to the surface bath; skimming off the wax; draining the product from the second bath; and stirring it in a third bath comprising an aqueous solution containing from about 0.4% to about 1.0% of an organic sulfonated wetting-detergent-scouring agent equivalent to that used in the first treating bath and a strong inorganic acid to yield a pH number of about 1.3 to about pH 2, at a temperature of from about 70° C. to about 100° C., for approximately one hour; stirring the product in a fourth bath similar to the second one; and finally rinsing the wax-free paper product with water.

4. The process for reclaiming wax-paper products which comprises, in combination, digesting a quantity of such product in a first bath comprising an aqueous solution containing from about 0.4% to about 1.9% of an alkyl aryl sulfonate and a strong inorganic acid to yield a pH number of from about pH 1.3 to about pH 2, at a temperature of from about 70° C. to about 100° C., for from about fifteen minutes to about five hours, whereby the waxy constituent is for the most part separated from the product, and rises to the surface of the bath; skimming the wax from the surface; draining the product from the first bath, and treating it in a second bath comprising an aqueous solution containing from about 0.03% to about 0.2% of a gas evolving bleaching agent at approximately 70° C., for from about ten minutes to about fifteen minutes, whereby remanent wax is dislodged from the product and rises to the surface bath; skimming off the wax; draining the product from the second bath; and treating it in a third bath comprising an aqueous solution containing from about 0.4% to about 1.0% of an alkyl aryl sulfonate and a strong inorganic acid to yield a pH number of from about pH 1.3 to about pH 2, at a temperature of from about 70° C. to about 100° C., for approximately one hour; and finally rinsing the wax-free paper product with water.

5. The process for reclaiming wax-paper products which comprises, in combination, digesting a quantity of such product in a first bath comprising an aqueous solution containing from about 0.4% to about 1.9% of a saturated hydrocarbon sodium sulfonate and a strong inorganic acid to approximately pH 2 to about pH 1.3, at a temperature of from about 70° C. to about 100° C., for from about fifteen minutes to about five hours, whereby the waxy constituent is for the most part separated from the product, and rises to the surface of the bath; skimming the wax from the surface; draining the product from the first bath, and treating it in a second bath comprising an aqueous solution containing from about 0.03% to about 0.2% of a gas evolving bleaching agent at approximately 70° C., for from about ten minutes to about fifteen minutes, whereby remanent wax is dislodged from the product and rises to the surface bath; skimming off the wax; draining the product from the second bath; and treating it in a third bath comprising an aqueous solution containing from about 0.4% to about 1.0% of a saturated hydrocarbon sodium sulfonate and a strong inorganic acid to approximately pH 2 to about pH 1.3, at a temperature of from about 70° C. to about 100° C., for approximately one hour; and finally rinsing the wax-free paper product with water.

HENRY B. HOPE.

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