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DECOLORIZING PAPER STOCK

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This invention relates to the decolorizing of paper stock to prepare it for use in making paper.

Used and waste paper, rags, and the like cellulosic materials adapted to paper manufacture form one source of paper stock. Where high-grade papers, such as ledger paper, are to be made, and where the materials carry or contain colorants such as inks and dyes, it is necessary to subject such raw materials or stock to a decolorizing operation. Thus, waste ledger paper carries the inks used in lining the paper and in making entries, and rags and colored "broke" generally carry substantial proportions of dyes, so that such materials are not adapted to the production of high-grade white papers unless the colorant is first removed. Heretofore decolorizing of paper stock has been effected generally by cooking it with a solution of an alkali. For reasons of economy the alkalies used are usually caustic soda, soda ash and the like. Such practices are used extensively in the art and understood by those familiar with it. All paper stock materials of the class referred to have not been available for the manufacture of ledger, book, and other high-grade papers according to the previously known procedures because some of the colors encountered have been difficult to bleach or even unbleachable, either practically or economically. As an example, paper which has been printed by the so-called "Vaporin Ink" process has been considered to be unsatisfactory for the manufacture of high-grade papers because it has not been amenable to the decolorizing processes known and used prior to the present invention. Also, the dye or pigment content of fast color rags and most colored "broke" has been so resistant to conventional decolorizing processes as to render this source of paper stock unsuited to the manufacture of high brightness white papers.

Ordinary printing inks used in conventional printing processes comprise pigment and a relatively slow drying oil so that they dry at a comparatively slow rate. Rapidity of ink drying is the underlying essential of the procedure referred to as the "Vaporin Ink" process. In this and similar procedures there are used the so-called "flash inks" which, to expedite their rate of drying, contain driers such as manganese or cobalt resinate or linoleate. To the same end, they may also contain such materials as nitrocellulose compounds. Also, the inked paper is exposed immediately after printing to supernormal temperatures, as by being passed through a tunnel over a flame.

Also, in the manufacture of paper board and the like there may be used as a raw material old corrugated paper boxes. Such materials frequently contain asphalt, either carried in sealing tape or contained in the paper stock. When paper board is made from such raw material the asphalt agglomerates and forms black spots through the sheet which render it of objectionable appearance.

Major objects of the invention are to provide a process of decolorizing paper stock which efficiently, economically and rapidly effects satisfactory decolorizing of paper stock, particularly stock carrying colorants difficult to bleach or unbleachable by the procedures known prior to the present invention; which is applicable generally to paper stock materials including, for example, waste paper, colored broke, and colored rags, especially those dyed with fast colors such as vat dyes, to prepare them for use in the making of high-grade white papers; which produces stock of lighter color as it comes from the boiler than has heretofore been generally possible; and which may effect economies in bleaching.

Another object is to provide a process of preparing paper-board stock from waste paper board or the like which carries or contains asphalt or the like hydrocarbonaceous material whereby easily, cheaply and effectively to remove the asphalt or render it unnoticeable.

The invention is predicated upon my discovery that its stated objects are attained by the use of divalent nickel (Ni^{++}) compounds in conjunction with alkaline decolorizing procedures. An important feature of the invention is intimate and uniform dispersion of the nickel reagent through the stock being treated, and such dissemination of the reagent is ordinarily attained more readily by the use of a water-soluble nickel salt. Such a nickel salt may be distributed intimately and uniformly throughout the stock prior to the introduction of the alkali bath. Various nickel salts are suited for this purpose, examples being the chloride and the sulfate. The ordinary hydrated commercial salts (e. g., $NiCl_2.6H_2O$; $NiSO_4.7H_2O$) are entirely suited to the purposes of the invention. As far as I have been able to ascertain any nickelous salt can be used.

The gist of the invention therefore resides essentially in the addition of such a nickel compound or compounds to the conventional decolorizing processes using soda ash or caustic soda, which may, in some instances, be conducted otherwise without change, or without material change, from existing practice. It is desirable

that the nickel precipitate resulting from the alkali present, which appears unchanged at the end of the cooking operation, be removed from the pulp or stock prior to bleaching. If the nickel compound is permitted to remain in the stock it may exert a catalytic effect in the bleaching step resulting in excessive use of chlorine or other bleaching agent, and possibly in degradation and darkening of the pulp. In most instances it is desirable, therefore, that after the cooking operation the stock be washed thoroughly to remove the contained nickel compound.

The amount of nickel salt used will be dependent largely upon the particular material being treated and the content and character of its colorant. For example, more nickel compound may be necessary in the treatment of waste paper printed by the "Vaporin Ink" process than with waste ledger paper, not only because of the greater content of ink or dye, but also because of the more resistant nature of such printing inks. Enough nickel compound must be present, however, to effect breakdown of the colorant so that the color can be removed from the stock. In general, rather low concentrations suffice, even for treating materials that could not be decolorized satisfactorily before this invention. And while I am not aware of any critical upper limit, the maximum amount of nickel compound should be kept as low as practicable for reasons of economy. In tests of the process on a commercial scale I have found that in general from about 7.5 to 20 pounds of ordinary hydrated nickel sulfate ($NiSO_4.7H_2O$) per ton of dry stock suffices, i. e., about 0.375 to 1.0 per cent of the salt by weight.

For maximum rapidity and completeness of decolorizing it is important that the nickel compound be intimately dispersed throughout the stock. To this end it may be added in the alkaline cooking bath which is thoroughly mixed with the stock as by continued agitation. For most purposes it is preferred in practicing the invention to distribute the nickel compound through the stock prior to the introduction of alkali. This may be done, for instance, by adding an aqueous solution of nickel salt to the stock and then subjecting the mixture to agitation and a short cook to cause the stock to be thoroughly impregnated with the nickel salt solution. Thereafter the alkali cooking bath is introduced, whereupon the nickel precipitate produced thereby is dispersed throughout the body of the stock, thus insuring the completion of rapid and efficient decolorization.

While ordinary alkali cooking baths may be used, such as plain solutions of caustic soda (NaOH) such as used heretofore, particularly when ridding paper-board stock of asphalt, experience has shown that in using caustic soda or soda ash alone in the making of high-grade paper stock the nickelous hydroxide tends to adhere rather tenaciously to the pulp, thus impeding thorough washing and enhancing the possibility of carrying nickel over into the bleaching operation with the undesirable consequences alluded to hereinabove. I have discovered, however, that this disadvantage is repressed or eliminated by the use of an alkali cooking bath containing an alkali silicate, most suitably sodium silicate ($xNa_2O.ySiO_2$). When alkali solutions containing such silicates are used in the practice of the invention the nickel precipitate formed seems to be deflocculated by the silicate or otherwise conditioned or modified so that it is readily removed by simple washing operations. The use of silicate appears to be unnecessary, however, in removing asphalt from paper-board stock.

As in the case of nickel compound, the concentrations of alkali, or of alkali and silicate, will vary according to the material being treated, i. e., according to whether the stock consists of colored rags, colored "broke," or waste paper, as well as upon the particular inks and dyes which must be eliminated. In general, however, the cooking solutions used for decolorizing may be used in the practice of the invention and altered in accordance with the stock being treated and the particular preferences of individual operators. The ratios of Na_2O to SiO_2 in the alkali-silicate compositions may be varied, generally speaking, within rather wide limits, particularly since both the alkali and the alkali silicate exert a destructive action upon the binder, such as varnish, used in printing inks.

In the practice of the invention an elevated temperature is necessary to effect substantial breakdown and removal of the colorant. Generally speaking, the temperatures ordinarily used in conventional decolorizing processes involving cooking with an alkali solution are effective and suitable in the practice of this invention. Preferably the temperature should be at least about 175° F. and in the range used in commercial decolorizing cooking, say up to about 300° F. or perhaps higher. The temperature should not be such, however, as itself to deteriorate the stock or to cause degradation by the cooking bath.

The invention may be further understood with reference to the following example. From 4500 to 5000 pounds of air dry mixed colored ledger stock are shredded, dusted, and packed dry into a rotary boiler of the type in common use in paper mills. 7.5 pounds of nickelous sulfate ($NiSO_4.7H_2O$) per ton of paper are then dissolved in hot water, say at 150 to 170° F., and introduced into the boiler. Water is then added, and after the boiler has been closed rotation is commenced and steam turned on. The steam pressure in the boiler is allowed to reach 25 pounds per square inch, and the boiler is rotated at this pressure for one-half hour. This step effects distribution of the nickel salt throughout the charge of paper.

The steam is then blown off, without appreciable loss of the cooking liquor, to bring the boiler pressure to atmospheric, and a mixture of caustic soda and sodium silicate in the proportions of 35 pounds of caustic soda to 100 pounds of 40° Baumé sodium silicate, previously dissolved in hot water, is injected into the boiler. For the best results these steps should be so performed as to avoid, as far as possible, introduction of air into the boiler because oxidation of the nickel compound may impair the results. Most advantageously no air is allowed to enter the boiler from the time the cook is started until the hot, cooked stock is dumped. The boiler is again rotated with steam turned on and the charge cooked for 8 hours at 25 pounds per square inch steam pressure. At the end of that time the steam pressure and cooking liquid are blown off, any residual cooking liquor being allowed to drain off as far as possible.

The cooked stock is then dumped and fed into a beater of the usual type in which it is mixed with fresh water, steam being applied to bring the pulp-water mixture to a temperature of, for

example, 160 to 180° F. Beating is continued in this manner for 1½ hours. The ensuing beater treatment effects defibering and completes the de-inking of the wads or masses of undefibered paper which during cooking were not defibered and thus exposed to the action of the reagent and which may thus contain amounts of ink and dyes not acted upon or not fully acted upon in the cooking operation. By such defibering the de-inking is rendered complete. After beating the pulp is treated in conventional manner, as by being diluted with water, jordaned, screened, washed on a conventional three-cylinder washer, and bleached, as with calcium hypochlorite.

In the foregoing example, as will be observed, the nickel salt is added to the paper stock with the water used to wet it. It is possible, of course, to wet the stock and then introduce the nickel salt, either as a solid which becomes dissolved and distributed through the mass, or as a solution in water or in the alkali cooking bath, as indicated hereinabove. I have found, however, that where the stock is wet the nickel compound should be added either at the same time or quite promptly thereafter to obtain the most satisfactory results. For example, if the stock is wet with water and allowed to stand for some hours, say over night, prior to adding the nickel compound, the stock is not decolorized to as satisfactory an extent as where it is wet and treated either concurrently or promptly thereafter with the nickel compound.

Various advantages accrue from the practice of the invention. A major advantage is that inks and dyestuffs, especially some red and blue dyes, which heretofore were not decolorized, or were decolorized unsatisfactorily, are rapidly decolorized with production of stock of satisfactory whiteness. Dyestuffs which have only been partly acted upon by the reagents used in prior practice are more completely decolorized so that the final bleaching operation achieves complete decolorizing such as not attained heretofore in the case of such dyestuffs. Generally speaking, the pulp as dumped from the boiler is lighter in color than attained by procedures not involving the use of nickelous reagent, and this in turn produces economy through reduction in the bleach liquor consumption necessary to attain a pulp of given brightness. Also, the inks are more thoroughly and more quickly acted upon by the cooking reagent. The net result is the production of paper stock adapted for the production of paper of higher color, greater strength, and greater permanency, than has heretofore been possible from the same raw materials, and the applicability of the invention generally to waste materials adapted to the manufacture of paper stock.

While not restricting myself to this theory, I now believe that the nickelous salts have a specific catalytic action on cobalt and similar driers as well as upon organic dyes present in the inks or otherwise carried by the stock undergoing treatment.

The invention may be illustrated further by reference to its application to the removal of asphalt from paper-board stock, in which the principles explained above seem equally to apply. By treating such stock with nickelous compounds in accordance with the invention the asphalt is acted upon in such manner that it is disseminated so finely through the stock as not to cause spotting, or it can be washed entirely from the stock.

For instance, the stock and an aqueous solution of nickelous salt are agitated, as in a conventional paper mill beater, while heating to a minimum of about 175° F. After a short boil caustic soda is added, and the mixture is again boiled to permit action of the nickel compound upon the asphalt. The pulp can then be used in the manner customary in paper-board mills without formation of black spots, or, if desired, it can first be washed free from the dispersed asphalt in any conventional manner.

For the best results in practicing the invention air and other oxidizing agencies should be excluded during the treatment with the nickel salt. For this reason the relatively high temperatures referred to are desirable, because their use tends to eliminate air from the cooking liquor.

According to the provisions of the patent statutes, I have explained the principle and mode of practicing my invention and have described what I now consider to represent its best embodiments. However, I desire to have it understood that, within the scope of the appended claims, the invention may be practiced otherwise than as specificaly illustrated and described.

I claim:

1. In a method of treating paper stock with an aqueous alkaline solution to condition the stock for use, the step of effecting such treatment in the presence of a nickelous compound and thereby effecting loosening of coloring agents carried by the stock.

2. In a method of treating paper stock with an aqueous alkaline solution to condition the stock for use, the step of effecting such treatment in the presence of a nickelous compound and in the substantial absence of air, and thereby effecting loosening of coloring agents carried by the stock.

3. That method of decolorizing paper stock which comprises the steps of treating such stock with an alkaline solution containing a nickelous compound, subjecting the mixture to an elevated temperature, and washing to remove undesired matter from the stock.

4. That method of decolorizing paper stock which comprises the steps of treating such stock with an alkaline solution containing alkali silicate and a nickelous compound, subjecting the mixture to an elevated temperature, and washing to remove undesired matter from the stock.

5. In a method of decolorizing paper stock with an aqueous alkaline solution, the step of dispersing throughout the stock, prior to the addition of said alkali, a nickelous compound.

6. That method of decolorizing paper stock which comprises the steps of mixing such stock with an aqueous solution of a nickelous compound, heating the mixture and agitating it to produce uniform dispersion of nickel compound throughout the stock, then adding a solution of an alkali and an alkaline silicate, continuing the heating and agitation to effect decomposition of color, and then washing to remove nickel from the stock.

7. A method according to claim 6, said compound being nickel chloride.

8. A method according to claim 6, said compound being nickel sulfate.

9. A method according to claim 6, the treatment being effected in the substantial absence of air.

10. That method of decolorizing paper stock which comprises the steps of wetting the stock with water, promptly mixing the wet stock with a nickelous compound, adding a solution of an alkali and an alkali silicate, heating and agitat-

ing the mixture to produce uniform dispersion of nickel compound throughout the stock and decomposition of color, and then washing to remove undesired matter from the stock.

11. A method of treating paper-board stock which carries asphalt to condition the stock for reuse, comprising the steps of cooking the stock while agitating it in the presence of an alkali, water and a nickelous compound to effect loosening of the asphalt.

12. In a method of treating paper stock with an aqueous alkaline solution to condition the stock for use, the step of effecting such treatment in the presence of nickelous hydroxide and in the substantial absence of air, and thereby effecting loosening of coloring agents carried by the stock.

13. In a method of decolorizing paper stock with an aqueous alkaline solution, the steps comprising uniformly dispersing nickelous hydroxide throughout the stock, heating and agitating the stock in contact with said nickelous hydroxide while suspended in said aqueous alkaline solution to effect separation of coloring matter from the stock, and then washing to remove nickel from the stock.

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