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3,284,229

MANUFACTURE OF COLORED CELLULOSE SPONGE

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This invention relates in general to the manufacture of colored cellulose sponge which has been impregnated with a polyhydric alcohol or other suitable sponge-softening material, and in particular to a new method of making such sponge in colors having improved brilliance or brightness characteristics.

The term "sponge" designates a product made of porous sponge-like material in any size or shape, for example, a block having a volume of over a cubic foot, a block to fit the hand or a mop, a sheet only a fraction of an inch thick, or in the form of a coating on mop yarn.

The term "colors" designates both chromatic colors (e.g. pink, green, and purple) and achromatic colors (e.g. white and off-white).

Colored cellulose sponge products containing a softening agent have become very popular merchandise. The softness and compressibility resulting from the presence of softening agent appeal to the customer's sense of touch. And the color, of course, enhances the eye-appeal of the products, particularly when the color has good brilliance. But prior to the present invention, sponge producers have found it difficult to produce softener-treated sponge at reasonable cost in colors having both a high degree of brilliance and good uniformity of brilliance (uniformity in a given batch and uniformity over a series of batches).

The problem of unsatisfactory brilliance is especially serious when the pore-forming salt employed in making the sponge material has been used repeatedly in sponge manufacture; that is, when the salt crystals have been extracted from previous batches of the product, recrystallized, and used again and again in making more sponge.

It is highly desirable for economic reasons to make repeated use of the pore-forming salt. However, despite the use of well-known salt purification procedures, increasing amounts of sponge-darkening contaminants accumulate in the salt, for example, lignin and sulfur compounds such as trithiocarbonates, sodium sulfide and sodium polysulfides. Cellulose, flax and like raw materials are known to be sources of these contaminants. Such contaminants also accumulate in the sponge-softening bath, causing the bath to appear dark and dirty. As these contaminants are introduced into the sponge by the salt and/or the softening bath, successive batches of sponge become less and less brilliant and increasingly dingy, gray and dirty in appearance.

Prior art sponge brightening methods leave much to be desired. For example, it has been proposed to dip the cellulose sponge in a sodium hypochlorite bleach solution, rinse out and neutralize residual bleach, and then dip the product in a softener solution. But this method offers no control over the loss of brilliance which results from the use of a softener bath containing an accumulation of brilliance-reducing contaminants and the hypochlorite tends to degrade the cellulose in the product. On the other hand, bleaching with hypochlorite after the sponge is impregnated with softener is impractical because of softener removal and reaction of the softener with hypochlorite.

It is therefore an object of this invention to provide a new and improved method of making colored, softener-impregnated cellulose sponge products.

It is also an object to provide a method adapted for the manufacture of such products in colors having improved uniformity and brilliance.

Other objects will be apparent from the description of the invention which follows.

Expressed broadly, the method of this invention comprises impregnating colored cellulose sponge with a liquid composition comprising a sponge-softening material and hydrogen peroxide until the brilliance of the sponge is improved. Under the more common production conditions, such as those in the examples, the liquid composition should have a hydrogen peroxide content, calculated as 100% H_2O_2 , of about from 0.004–0.2% by weight.

In preferred embodiments of the method, the liquid composition contains a substantial percentage of water, and the sponge is dried in a heat zone or other means suitable for removing all or most of the water and any other material more volatile than the softener (e.g., residual hydrogen peroxide).

The colored cellulose sponge can be made by any known method for producing such a material. A typical method of making cellulose sponge comprises the steps of

(a) treating wood pulp sheets with sodium hydroxide to form alkalicellulose,

(b) treating the alkalicellulose in crumb form with carbon bisulfide to form sodium cellulose xanthate,

(c) mixing the sodium cellulose xanthate with water or dilute sodium hydroxide to form viscose,

(d) mixing the viscose with a pore-forming material, for example, Glauber's salt crystals,

(e) introducing the mixture into a mold of any desired shape,

(f) coagulating the mixture under conditions which regenerate the cellulose, and

(g) extracting the pore-forming material to yield a porous, sponge structure of regenerated cellulose.

The resulting sponge material is cut to dimensions appropriate for the use intended.

Such a method is disclosed in further detail in U.S. Patent 2,280,022.

During step (d), it is preferred to add to the viscose a fibrous strength-giving material such as fibers of cotton, hemp, flax or rayon.

During step (d) is also a convenient time to add coloring matter, for example, a pigment or a dye. One method of adding coloring matter to the viscose is by using colored fibers. A preferred method is to add the coloring matter to the viscose as a pigment dispersed in a volatile liquid, the dispersion also containing a water-insoluble film-forming material. Coloring matter can also be incorporated at any other convenient time, for example, by dyeing the sponge structure resulting from step (g).

Coagulation (step f) is preferably accomplished by the method described in U.S. Patent 2,133,810, wherein coagulation is brought about by the heat produced in the mixture by its resistance to an electric current. The teaching of U.S. 2,133,810 is incorporated herein by reference.

As indicated in step (g), the coagulated spongy cellulose structure is washed with water until free of Glauber's salt or other pore-forming material. Much of the water can then be removed from the sponge by squeezing or vacuum draining it.

Either before or after the resulting washed sponge is dried (preferably before), it is impregnated with a liquid composition (impregnant) comprising a sponge-softening material and hydrogen peroxide until the brilliance of the sponge is improved. The impregnant preferably has a hydrogen peroxide content, calculated as 100% H_2O_2 , of about from 0.004–0.2% by weight, and still more prefer-

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ably about from 0.02–0.05%. The latter range (0.02–0.05%) usually gives the best balance of brilliance characteristics and reasonable production costs. A satisfactory improvement in brilliance is not obtained at less than about 0.004% hydrogen peroxide in the impregnant except under special circumstances, for example, by subjecting the sponge to a series of impregnating cycles. More than about 0.2% hydrogen peroxide tends to cause some degradation of the cellulose with resultant reduction in sponge durability. Degradation can be avoided or minimized, however, at slightly above 0.2%, by permitting the impregnant to remain in contact with the sponge for an extremely short period of time; for example, by rapidly squeezing and drying the sponge after wetting it with impregnant. Over 0.2% also adds unnecessarily to the cost and produces little if any additional brilliance. The hydrogen peroxide is preferably added to the softener material as an aqueous solution, for example, a 30% solution.

The rate of consumption of hydrogen peroxide in this method is surprisingly low and the stability of the impregnating bath is surprisingly good when successive batches of sponge products are immersed in the bath.

Sufficient softening material is deposited in the sponge to render it soft and compressible. The best amount of softener to be deposited will be governed by such factors as how hygroscopic the softener is and the degree of softness desired. With the preferred polyhydric alcohols, best results are usually obtained when about from 15 to 50% of softener by weight of dry cellulose in the sponge is deposited in the sponge. The preferred softener component has a polyhydric alcohol content of over 50 weight percent.

The useful sponge-softening materials are exemplified by glycerine, ethylene glycol, diethylene glycol, propylene glycol, sorbitol and other polyhydric alcohols. The preferred softening agents are hygroscopic, and are therefore sometimes referred to as "humectants" or moisture conditioners. Urea is another preferred ingredient of the impregnant since it enhances the stability of the impregnant with respect to the hydrogen peroxide and it enhances the softening effect on the sponge by the polyhydric alcohols.

The blend of hydrogen peroxide and sponge-softening material is preferably dissolved or dispersed in liquid more volatile than the softener, for example, water, before it is introduced in the sponge. However, an impregnant consisting only of hydrogen peroxide and softener can also be used.

The impregnation of the sponge with the liquid composition can be accomplished by any known method of applying liquids to porous structures. For example, the sponge can be immersed in the composition, or the composition can be poured, rolled, spread or sprayed onto the sponge. The immersion method is usually the most practical; however, another method might be preferred in a certain application, such as where it is desired to keep one side of the sponge free of softener or moisture.

The impregnated sponge can, of course, be squeezed or vacuum drained in order to control the amount of impregnant actually deposited therein.

The impregnated sponge is dried in an oven, dielectric dryer, vacuum chamber or other means adapted to remove water and/or other material more volatile than the softener. Any excess hydrogen peroxide is readily decomposed and driven off during this step.

Among the advantages obtainable by the method of this invention in the manufacture of colored, softener-treated cellulose sponge products are the following:

The sponge has greater brilliance of color.

The sponge has better uniformity of color brilliance within a given batch and in successive batches.

Good brilliance is obtained even when the pore-forming salt and softener bath are used repeatedly.

No separate bleaching, bleach-neutralizing or bleach-rinsing step is necessary.

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It is quite unexpected that these advantageous results are achieved (a) with such a small concentration of hydrogen peroxide and (b) by introducing the hydrogen peroxide into the sponge along with the softener, and although the addition of hydrogen peroxide to a dark and dirty softener bath does not noticeably change the color of the bath, it very distinctly improves the brilliance of sponge treated with the bath—this is indeed surprising.

The method of this invention is useful for the manufacture of sponge products for scrubbing and wiping applications in homes, boats, factories, institutions and the like, and for the additional uses listed in U.S. Patent 2,295,823 (beginning on page 5, column 1, line 50).

The examples which follow are given for the purpose of illustrating the invention. All quantities shown are on a weight basis unless otherwise indicated.

EXAMPLE I

A sponge-forming mixture is prepared by thoroughly mixing 18.9 parts of a viscose/fiber composition with 100.4 parts of Glauber's salt crystals and 0.33 part of a yellow pigment dispersion.

The viscose/fiber composition is made up of 10.0% cellulose, 2.4% flax fiber, 5.7% sodium hydroxide, 6.0% carbon bisulfide and 75.9% water.

The salt crystals contain enough sponge-darkening contaminants to cause a marked darkening of sponge material made with them in the absence of a brightening agent. They have been subjected to many cycles of use in sponge production, each cycle including the extraction and recrystallization of the salt crystals.

The pigment dispersion consists of 2.4% benzidine yellow pigment, 4.0% acrylic resin and 93.6% water. The acrylic resin is an interpolymer of ethyl acrylate, methyl methacrylate and methacrylic acid prepared as described in U.S. Patent 2,795,564, Example I.

The sponge-forming mixture is introduced into a mold of desired size and shape and coagulated by the electrical resistance method described in the example given in U.S. Patent 2,133,810. The heat generated by the electrical resistance of the mixture during coagulation causes the salt crystals to melt and form a solution with the water present in the structure. A porous, sponge structure of regenerated cellulose is thus produced in the mold.

The sponge is washed with water until free of Glauber's salt, squeezed by means of rollers to remove excess water, and then immersed for 10 minutes in an impregnating composition containing softener and hydrogen peroxide at a temperature of 55° C. The impregnating composition, which is freshly made and substantially colorless, consists of 6.25 parts of hydroxypropyl sorbitol, 10.50 parts of diethylene glycol, 6.75 parts of urea, 0.25 part of dihydroabietyl amine, 0.25 parts of Arquad-16, 0.03 part of hydrogen peroxide and 75.97 parts of water. The hydrogen peroxide content is given on the basis of 100% H₂O₂, although added in the form of a 30% solution in water. Arquad-16, from Armour and Company, is understood to be an alkyl trimethyl ammonium chloride containing 90% hexadecyl ammonium chloride, 6% octadecyl trimethyl ammonium chloride and 4% octadecenyl trimethyl ammonium chloride.

The sponge has a dirty yellow color just prior to its immersion in the impregnating composition. Almost instantly upon being wet with the composition, it shows a pronounced improvement in color brilliance.

Upon its removal from the impregnating bath, the sponge is passed between squeeze rolls to remove excess impregnant. The sponge now has an impregnant content of 2.5 times the weight of cellulose (dry basis) in the sponge.

Substantially all of the water and residual hydrogen peroxide is removed from the sponge by passing it through a heat zone having an ambient temperature of 100° C. The sponge is then cut into pieces of suitable dimensions for use by the householder or other consumer.

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The sponge material produced in this example has a uniformly brilliant yellow color throughout its structure. It also has good softness and compressibility, and normal durability.

A control sample of sponge is prepared by repeating Example I except for the omission of hydrogen peroxide from the impregnating composition. Since the resulting sponge has a dingy yellow color, it has considerably less eye appeal than the product of Example I. The tensile strength and abrasion resistance are substantially the same as for the product of Example I.

EXAMPLE II

This example illustrates the repeated use of pore-forming salt and impregnating bath in the mass production of household sponges by the method of this invention.

Example I is repeated 50 times in rapid succession without making up a fresh impregnating bath. Each mold has a volume of over one cubic foot. After each batch of sponge is impregnated, a quantity of fresh impregnating composition equal to the amount removed by the sponge is poured into the impregnating bath. Also, enough additional hydrogen peroxide is added to replace the amount consumed by the previous bath and to maintain the hydrogen peroxide content of the impregnant at about 0.03% of 100% H_2O_2 . For each 100 pounds of sponge (dry cellulose content) treated in the impregnating bath, only 0.75 pound of 30% H_2O_2 (0.225 pound of 100% H_2O_2) is consumed.

During the production of these 50 batches of sponge material, the impregnating bath becomes very dark and dirty in appearance. But all 50 batches of the product surprisingly have substantially the same brilliant yellow color and other properties as the product of Example I.

I claim:

1. In a method of making colored cellulose sponge of

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improved brilliance, the improvement consisting essentially of impregnating colored cellulose sponge with a liquid composition consisting essentially of a sponge-softening material and hydrogen peroxide until the brilliance of the sponge is improved, said liquid composition having a hydrogen peroxide content, calculated as 100% H_2O_2 , of about 0.004 to 0.2% by weight.

2. A method as defined in claim 1 wherein said liquid composition contains contaminants which would darken the color of the sponge in the absence of said hydrogen peroxide.

3. A method as defined in claim 1 wherein a major proportion of said sponge-softening material consists of a hygroscopic polyhydric alcohol.

4. A method as defined in claim 3 wherein said liquid composition is an aqueous solution of the sponge-softening material and hydrogen peroxide.

5. A method as defined in claim 4 wherein said hydrogen peroxide content is about from 0.02–0.05%.

6. A method as defined in claim 4 wherein the resulting impregnated sponge is passed through a heat zone to remove water and residual hydrogen peroxide.

References Cited by the Examiner

UNITED STATES PATENTS

2,295,823	9/1942	Banigan et al.	
2,418,660	4/1947	O'Shaughnessy.	
2,698,625	1/1955	Bitzer	8—137.5 X
2,945,772	7/1960	James	117—98
3,057,745	10/1962	Meador	106—287

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