This invention relates to alkaline aqueous media of improved wetting, penetrating and dispersing powers, more particularly baths for the treatment of cellulosic fibers, and a process for the production thereof.

It is known that the ordinary soaps of commerce such as sodium oleate, sodium stearate, and similar compounds are good wetting agents in distilled water and also have some wetting power in dilute alkaline solutions. In strong alkaline solutions, however, such as those of mercerizing strength, they are of little practical value because the high concentration of alkali has a tendency to salt them out of solution, and if they have any useful effect it is only for a very short time.

An object of this invention is to produce alkaline aqueous media characterized by improved wetting, penetrating and dispersing properties. A further object is the production of alkaline aqueous baths for the treatment of textile materials. A still further object is to produce aqueous baths which are relatively concentrated in alkaline reacting substances and yet possess marked wetting, penetrating and dispersing characteristics. A more specific object is the production of relatively concentrated solutions of alkaline metal hydroxides which possess improved wetting, penetrating and dispersing powers and are especially well adapted for the treatment of cellulosic materials. Another object of the invention is to produce baths highly efficient for the mercerization of cotton materials. A further object is to produce baths which are efficient to such an extent that unboiled or grey cotton may be mercerized directly by treatment therewith. A still further object is the provision of new and improved processes for producing products of the character above described. Other objects will appear hereinafter.

These objects are accomplished according to the invention by adding or forming in strongly alkaline aqueous media a penetrating agent comprising a soluble salt of a branched chain aliphatic carboxylic acid having at least five and preferably six to ten carbon atoms. We have found that these branched chain acids possess excellent wetting power in the presence of strong alkalis, as, for instance, mercerizing baths; and, because of their greater solubility, do not precipitate out of solution like the straight chain acids.

In practising the invention, we prefer to employ strongly alkaline solutions containing as penetrating agents the water-soluble salts obtainable by the caustic dehydrogenation of substantially water-insoluble higher fractions of oxygenated organic compounds resulting from the catalytic hydrogenation of oxides of carbon under high pressure. A method of synthesizing such oxygenated organic compounds is described in a U. S. patent to Roger Williams, No. 1,820,417. These fractions have defied complete analysis, but are known to contain chiefly branched chain aliphatic alcohols, both primary and secondary, and are therefore herein referred to as "higher alcoholic fractions."

When the substantially water-insoluble "higher alcoholic fractions" are heated with caustic alkaline solutions in an autoclave under elevated temperature and pressure conditions, the primary and secondary chain alkali salts are converted to the corresponding aliphatic carboxylic acid alkali metal salts which are water-soluble, while the secondary alkali salts apparently remain unreacted upon and, being water-insoluble, are readily removed from the desired water-soluble portion. This process, while usually referred to as "caustic dehydrogenation," may also be called "caustic oxidation."

A method of caustic dehydrogenation applicable to the conversion of the "higher alcoholic fractions" to water-soluble salts of branched chain aliphatic carboxylic acids is described in U. S. Patent No. 1,856,263. The caustic dehydrogenation may be effected, for example, by heating the "higher alcoholic fraction" in an autoclave with an aqueous caustic alkali solution having a concentration of about 15° Be. at a temperature of the order of about 300° C. and under autogenous pressure. The autoclave is then cooled opened and the aqueous portion of the reaction product containing the alkali metal salts of the branched chain carboxylic acids is separated from the water-insoluble portion consisting largely of secondary alcohols. The alkali metal salts of the branched chain carboxylic acids may be isolated as solids or they may be allowed to remain in the aqueous fraction directly obtained from the caustic dehydrogenation. In either case, they...
are then mixed with strong caustic alkalis and in this form exhibit marked wetting and penetrating properties.

The following table (Table I) will illustrate the type of “higher alcohol fraction” which may be subjected to caustic dehydrogenation and the nature of the branched chain carboxylic acids, or mixtures containing them, which are thus produced. Column 1 gives the boiling ranges of various “higher alcohol fractions” obtained by the catalytic hydrogenation of carbon monoxide under high pressure. Column 2 gives the chief primary alcohol component or components of said fraction. Column 3 gives the boiling point of said component or components. In Column 4 the approximate percentage composition of the “higher alcoholic fraction” is given. Column 5 illustrates the principal branched chain aliphatic carboxylic acid alkali metal salts present in the water-soluble portion of the reaction product after caustic dehydrogenation of the “higher alcoholic fraction” with caustic soda solution.

Table I

<table>
<thead>
<tr>
<th>Penetrating agent</th>
<th>Boiling range of fraction °C</th>
<th>Components</th>
<th>Boiling points of components °C</th>
<th>Approximate composition of fraction in %</th>
<th>Chief components of dehydrogenated products</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td></td>
<td>A</td>
<td>150-170</td>
<td>2.4-dimethyl pentanol-1</td>
<td>159.8, 255</td>
</tr>
<tr>
<td></td>
<td></td>
<td>B</td>
<td>160-170</td>
<td>4 - methyl hexanol-1, 2.4-dimethyl hexanol-1</td>
<td>165.0, 171.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>C</td>
<td>160-190</td>
<td>4-methyl hexanol-1, 2.4-dimethyl hexanol-1</td>
<td>165.0, 171.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>D</td>
<td>140-160</td>
<td>2-methyl pentanol-1, 4 - methyl pentanol-1, secondary alcohol</td>
<td>147.0, 145.6</td>
</tr>
</tbody>
</table>

* Including small amounts of primary alcohols and unidentified substances.

* Identification not conclusive.

Mixtures of the typical caustic dehydrogenation products described in Table I, with 15–35% aqueous caustic alkali, represent preferred compositions of this invention.

The efficiency of branched chain carboxylic acid salts of the type described above in increasing the wetting and penetrating power of strongly alkaline solutions was tested in mercerizing baths by comparing the speed of mercerization. The method employed was empirical and the results obtained were relative rather than absolute, but nevertheless of such character as to show the success of the invention.

The testing apparatus employed consisted of a glass cylinder, two inches in diameter by twenty inches in height, marked vertically in divisions of one-eighth inch each. In making the tests this cylinder was filled with mercerizing liquids containing various addition agents. Skeins of two-ply unboiled cotton yarns were suspended in the mercerizing liquids from a small wire hook attached to a rod which rested on the top of the glass cylinder. In each test a 25 gram weight was attached to the bottom of the skein by means of another wire hook. All of the skeins used were of exactly the same length so that the total length of the apparatus from the rod at the top to the bottom of the weight was the same in all tests. The length of the skeins and wires was such that the bottom of the weight was about an inch above the bottom of the cylinder.

Since shrinkage of the cotton fiber being mercerized is one of the characteristics of the mercerization process, the rate of shrinkage of the skein was measured. This was done by dropping the skein with weight attached into a given mercerizing liquor, and simultaneously starting a stop watch. The time required for a definite shrinkage (1½ inches) was measured by noting the time at which the weight had risen to a pre-determined mark. The time required in each case was, therefore, a measure of the relative efficiency of the mercerizing bath. For purposes of comparison, tests were made with a merceriz-
<table>
<thead>
<tr>
<th>Test No.</th>
<th>Mercerizing bath consisting of a 20% solution of sodium hydroxide as a penetrating agent</th>
<th>Concentration of penetrating agent in g/l</th>
<th>Mercerization time (seconds)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(A)</td>
<td>1.0</td>
<td>89.0</td>
</tr>
<tr>
<td>2</td>
<td>(B)</td>
<td>1.0</td>
<td>37.3</td>
</tr>
<tr>
<td>3</td>
<td>(C)</td>
<td>1.0</td>
<td>26.0</td>
</tr>
<tr>
<td>4</td>
<td>(D)</td>
<td>2.0</td>
<td>63.0</td>
</tr>
<tr>
<td>5</td>
<td>(E)</td>
<td>more than 15% above 10.0</td>
<td>60.0</td>
</tr>
</tbody>
</table>

It will be understood that the tests above are illustrative only and do not limit the invention as to the specific salts and proportions thereof as to the character of the alkaline media in which they are used.

While the salts, and mixtures containing the same, obtainable by the caustic dehydrogenation of "higher alcoholic fractions" are especially desirable, the invention is not limited to penetrating agents prepared in this manner. Similarly, while mixtures of salts of the type described have given the best results, individual salts of branched chain aliphatic carboxylic acids containing at least five carbon atoms and which are soluble to some extent in strongly alkaline aqueous solutions may be employed. The results obtained have demonstrated that the salts of branched chain aliphatic carboxylic acids containing 7 to 8 carbon atoms, and mixtures thereof, are superior to the other additional agents tested. Thus, while, in general, salts obtained by the caustic dehydrogenation of "higher alcoholic fractions" boiling in a range above about 140° C give good results, those from alcoholic fractions in which the boiling range starts around 150° C or around 160° C are especially desirable. The boiling range of other alcoholic fractions suitable for caustic dehydrogenation may extend higher than indicated in Table I, for example, to 200° C, 210° C, or even to 250° C, as long as material amounts of alcohols containing 6 to 10 carbon atoms are present.

The alkaline medium containing the penetrating agent should be strongly alkaline in order to secure the desired wetting and penetrating effect. By "strongly alkaline" is meant an alkalinity corresponding to at least 15% aqueous alkaline metal hydroxide solution. In general, solutions of mercerizing strength exhibit the most marked wetting and penetrating efficiency. The upper practical limit may vary and may be determined for any given penetrating agent by noting the salting-out effect of the alkalai. Usually, we prefer to employ solutions containing less than about 40% caustic alkalai. Ordinarily, within the preferred range of alkali concentration, the penetrating agents containing a lower number of carbon atoms are more useful with higher concentrations of alkali, and vice versa. It will be understood that the alkaline medium may contain more than one alkaline reacting substance, e.g., both sodium and potassium hydroxides.

The branched chain aliphatic carboxylic acid salts may be added to the alkaline media as such or formed therein, for example, by the addition of the free acids. In general, it is preferable to make the addition in the form of the dry alkali metal salts in paste form, or substantially concentrated aqueous solutions thereof. In mercerizing processes, the mercerization bath generally becomes more dilute as the mercerization proceeds. It is customary in such cases to maintain the concentration of the bath by the addition of relatively strong alkali metal hydroxide solutions. According to the present invention, the addition agents herein described can be included directly in such solutions. Instead of heating the bath, concentrated solutions of this character may be used in the initial preparation of the bath since they only require dilution to the proper concentration.

The proportions of penetrating agent introduced into a given alkali medium may vary within relatively wide limits depending largely upon the concentration of the alkaline reacting agent and the purpose for which the resultant product is to be employed. Thus, in the treatment of cotton fibers with mercerizing liquors the amount of penetrating agent employed will depend largely upon the degree of cleanliness of the fiber treated, the alkali concentration, the temperature of the bath, the count of the fabric (if in fabric form) and the rapidity of mercerization which it is desired to obtain. In general, however, larger amounts will be required with more greasy materials, with more tightly woven goods and with more dilute alkaline solutions. As a general rule, about 0.5 to 20.0 parts of penetrating agent per 1,000 parts of mercerizing liquor will give satisfactory results.

While the invention is preferably employed in the treatment of cellulosic fibers to effect penetration of a strong alkali, as in the mercerization of cotton fibers, fabrics and yarns, it may be employed for any purpose where it is desirable to have a strongly alkaline medium characterized by wetting, penetrating and dispersing powers. Ordinary or elevated temperatures may be used. It will be understood that alkaline aqueous media prepared in accordance with this invention may be employed in admixture with a wide variety of additional substances. As examples of such additional substances may be mentioned materials which possess or induce washing, cleansing, emulsifying, wetting, dispersing, adsorbing, lathering, or bleaching properties such as, for example, phenol and its homologues, benzy1 alcohol, butyl and amyl alcohol, the higher aliphatic alcohols (B.P. above about 120° C) obtained by the hydrogenation of carbon oxides (see also Table I above), the Turkey red oils, aliphatic and aromatic sulfonic acids such as alkylated naphthalene sulfonic acids, sulfonated derivatives of aromatic acid, sulfuri1 esters, sapponin, and aliphatic and aromatic acid amides, such as sodium taurocholate or sodium salts of analogous acid amides, sodium perborate, heterocyclic bases, and pine oil.

The principal advantage of the invention lies in the high wetting and penetrating efficiency of the products. Henceforth considerable difficulty has been encountered in the mercerization process because of the inefficiency of the removal of wax and grease from the fiber and resultant non-uniform mercerization. In the mercerization process as ordinarily conducted, the first step consists in cleaning the cotton by "boiling out", generally by means of a relatively dilute alkaline solution, to remove the grease from the surface of the fibers and permit the penetration of the alkaline liquid during the mercerization process proper. Unless the cleaning is carried out with due care so as to remove substantially all of the natural waxes and other water repellant material, the mercerization is uneven and results in fibers.
fabrics and yarns which cannot be dyed evenly. We have found that by employing mercerizing liquids containing soluble salts of the aforesaid branched chain aliphatic acids, the wetting and penetrating power of the bath is so great that the "boiling out" or purification process may be eliminated. In other words, by employing mercerizing liquids in accordance with our invention, unboiled or grey cotton may be mercerized directly, thereby saving the expense and trouble formerly involved in the purification prior to mercerization. Furthermore, by the application of the present invention more uniform mercerization and, hence, more even dyeing can be attained than has been possible heretofore. A further advantage of the invention lies in the small amounts of penetrating agent required which results from the greater efficiency of the agents described than those previously used.

The practice of the invention leads also to a more rapid mercerization, thereby effecting a greater economy of time than has been possible according to the prior art.

This application is a continuation-in-part of our U.S. application Serial No. 613,281 filed May 24, 1932.

As many apparent and widely different embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that we do not limit ourselves to the foregoing examples or description except as indicated in the following claims.

We claim:

1. In a process of treating cellulosic fibers with an alkaline aqueous medium containing about 15% to about 40% alkali metal hydroxide, the step which comprises improving the wetting, penetrating and dispersing power of said medium by including therewith an alkaline metal salt of a branched chain aliphatic carboxylic acid having six to ten carbon atoms.

2. The process of producing mercerized cotton materials which comprises treating cotton materials with an alkaline mercerizing bath containing a small amount of a mixture comprising substantially the sodium salts of branched chain aliphatic carboxylic acids having seven to eight carbon atoms.

3. The process of producing mercerized cotton materials which comprises treating cotton fibers, fabrics and yarns with an aqueous solution of an alkali metal hydroxide of mercerizing strength containing as a wetting and penetrating agent the water-soluble product comprising salts of branched chain primary aliphatic carboxylic acids obtainable by the caustic dehydrogenation of a higher alcoholic fraction containing material amounts of branched chain primary aliphatic alcohols having six to ten carbon atoms, resulting from the catalytic hydrogenation of oxides of carbon under high pressure.

4. In the process of producing mercerized cotton materials, the step which comprises subjecting grey cotton fibers, fabrics and yarns to treatment with a sodium hydroxide mercerizing bath containing as a penetrating agent a small amount of the water-soluble product comprising salts of branched chain primary aliphatic carboxylic acids, said product being substantially identical with that prepared by the caustic dehydrogenation of a higher alcohol fraction boiling from about 150° C. to about 160° C. obtained by the fractional distillation of the synthesis product of the reduction of carbon oxide with hydrogen.

5. A strongly alkaline medium of improved wetting, penetrating and dispersing power comprising an aqueous alkali metal hydroxide solution of mercerizing strength containing an alkali metal salt of a branched chain aliphatic carboxylic acid having six to ten carbon atoms.

6. An alkaline mercerizing bath containing as a wetting and penetrating agent the water-soluble product comprising salts of branched chain primary aliphatic carboxylic acids obtainable by the caustic dehydrogenation of a higher alcoholic fraction containing material amounts of branched chain primary aliphatic carboxylic acids having six to ten carbon atoms.

7. An alkaline mercerizing bath containing as a wetting and penetrating agent the water-soluble product comprising salts of branched chain primary aliphatic carboxylic acids obtainable by the caustic dehydrogenation of a higher alcoholic fraction boiling from about 150° C. to about 160° C. obtained by the fractional distillation of the synthesis product of the reduction of carbon oxide with hydrogen.

8. An alkaline mercerizing bath containing as a wetting and penetrating agent the water-soluble product comprising salts of branched chain primary aliphatic carboxylic acids obtainable by the caustic dehydrogenation of an alcoholic fraction boiling within the range of about 150° C. to about 160° C. obtained by the fractional distillation of the synthesis product of the reduction of carbon oxide with hydrogen.

9. An alkaline mercerizing bath containing as a wetting and penetrating agent the water-soluble product comprising salts of branched chain primary aliphatic carboxylic acids obtainable by the caustic dehydrogenation of an alcoholic fraction boiling within the range of about 150° C. to about 160° C. obtained by the fractional distillation of the synthesis product of the reduction of carbon oxide with hydrogen.

10. In a process of treating cellulosic fibers with a strongly alkaline aqueous medium to effect penetration of the alkali, the step which comprises reacting the cellulosic fibers with an alkaline aqueous medium comprising at least 15% of an alkali metal hydroxide and containing as a wetting and penetrating agent a small amount of the water-soluble product comprising salts of branched chain primary aliphatic carboxylic acids, said product being substantially identical with that prepared by the caustic dehydrogenation of a higher alcohol fraction boiling from about 140° C. to about 190° C. obtained by the fractional distillation of the synthesis product of the reduction of carbon oxide with hydrogen.

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RICHARD GESSE CLARKSON.