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PROCESS FOR PRODUCING NONSTICKING, SMOOTH, FLAMEPROOFED, THIN, FLEXIBLE SHEETING

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1 Claim. (Cl. 117—145)

This invention relates to flame-resistant sheet wrapping material, especially transparent flameproofed cellulosic web which, although it contains a softener, will not adhere to itself or other surfaces when subjected to pressure for considerable periods of time. More particularly it appertains to sizings for sulfamate impregnated films of regenerated cellulose and the like.

Recently there has appeared in commerce a transparent sheet wrapping material comprising a sheet of regenerated cellulose. The manufacture of such a sheet is described in U. S. A. Patent No. 1,548,864 (Brandenberger), and the impregnation thereof with a typical sulfamate flameproofing composition is described in U. S. A. Patent No. 2,142,116 (Cupery).

Unfortunately the addition of such substances to regenerated cellulose and the like induces a certain inherent stickiness or tackiness which causes layers of the impregnated material to adhere together rather firmly when subjected to pressure for relatively short periods of time. Stacks of sheets of such materials adhere with such tenacity that they cannot be readily separated for use. A similar disadvantage occurs in rolls of the material which have been stored for several days. They unroll with difficulty (due to adhesion of the film surfaces), and for this reason are unsatisfactory for operation upon automatic wrapping machinery, etc. Furthermore, sheet material of such a character adheres to the surfaces encountered in automatic machinery, and will not pass through such machinery with the facility requisite for smooth operation.

In spite of the many desirable characteristics of film impregnated with ammonium sulfamate and related sulfamic acid derivatives and a demand for such a material in certain fields its use has been restricted because of this marked tendency for the sheets to stick together and cake.

It has been suggested that this disadvantage of tackiness could be overcome by applying small amounts of suitable materials in a thin tenuous coating, for convenience called "sizes," to the surfaces of the webs to render them non-tacky. Years of reseach have, however, failed to reveal any substance which prevents (or materially reduces) sticking and which at the same time maintains the webs in transparent, haze-free, and otherwise satisfactory condition.

This invention has for an object the production of thin, non-fibrous, substantially nonporous sheets (films, foils) of improved resistance to sticking together with a minimum amount of haze or blush. Other objects were to produce transparent flameproofed regenerated cellulose sheet material which would not stick or cake, to produce sulfamate impregnated regenerated cellulose sheet which was non-tacky, to produce sizing emulsions or compositions stable in ammonium sulfamate solutions, to produce regenerated cellulose sheets having improved resistance to sticking together in atmospheres of high relative humidity and/or when improved with large quantities of softening material, and to produce non-sticking regenerated cellulose sheets impregnated with ammonium sulfamate. A general advance in the art, and other objects which will appear hereinafter, are also contemplated.

It has now been found that hard wax-shellac sizing compositions are stable in ammonium sulfamate and similar impregnating baths, and that thin sheeting may be sized with such materials with the result that the dried sheets do not stick together. More specifically it has been found that emulsions of carnauba wax and shellac may be placed on regenerated cellulose film which is wet with ammonium sulfamate solutions without being deleteriously affected and that such sheets when dried are found to be non-caking.

From the following description and specific examples, in which are disclosed certain embodiments of the invention as well as details of what is believed to be the best mode for carrying out the invention, it will be apparent how the foregoing objects and related ends are accomplished. The quantities are given by weight throughout the application unless otherwise specified.

Example I

A gel sheet formed, for example, as taught in U. S. A. Patent No. 1,548,864 (Brandenberger), by extruding viscose containing 7.5% cellulose and 6.5% sodium hydroxide through a long, narrow slit into a suitable coagulating bath and thereafter regenerating, desulfuring, bleaching, and washing, was conducted through a bath containing 7% ammonium sulfamate and 1.5% glycerol and a sufficient amount of the hereinafter described emulsion to give 0.5% solids.

The emulsion was made up by melting together at 90° C. 22.7 parts of carnauba wax and 9.7 parts of stearic acid. Then 8.9 parts of morpholine were added and the mixture stirred until clear. Hot water (203 parts) was added in small portions, with continuous stirring after each addition, until the water was completely dis-

persed. The emulsion was allowed to cool and 18.2 parts of bleached shellac dispersed in 2.4 parts of morpholine and 188 parts of water was added. To the mixture 2.3 parts of the sodium salts of a mixture of alkyl-phenyl sulfonates in which the alkyl substituents had 10 to 14 carbon atoms, were then added. Such emulsions have been found to give clear dispersions of excellent stability when added to the impregnating (softener) bath.

Films treated with this bath and then dried had good flame-resistance and were clear, smooth, non-tacky and durable. Furthermore, they did not stick or cake together when stored under pressure for considerable period of time, for example, for a week or more.

Example II

An emulsion was prepared by melting 22.4 parts of carnauba wax with 4.8 parts of oleic acid and 4.4 parts of morpholine. Hot water (134 parts) was dispersed in this melt in the same manner as in Example I. After cooling 3.0 parts of shellac dispersed in 0.4 part of morpholine and 31 parts of water were added. Sulfonated kerosene (1.8 parts) was added to the mixture. This emulsion when added to a 7% ammonium sulfamate solution so as to give 0.5% solids, produced a clear stable dispersion which was used to impregnate a gel regenerated cellulose film as in Example I.

The film so impregnated and dried in the usual manner, was highly flexible, transparent, durable and flame-resistant, and, furthermore, resisted sticking and caking together when stored under pressure for long periods of time.

Example III

A stick resistant emulsion was prepared by melting 14 parts of carnauba wax with 9 parts of triethanolamine oleate. Hot water (415 parts) was added and dispersed in the same manner as in Example I. Shellac (9 parts) dispersed in 5 parts of 23% aqua ammonia and 90 parts of water was added after cooling. Sulfonated kerosene (1.5 parts) were then added. This emulsion, when added to a solution containing 7% ammonium sulfamate and 1.5% glycerol in an amount to give 0.5 solids, gave a clear stable emulsion. Films treated with the bath were flame-resistant, soft, durable, clear and resistant to sticking.

The invention is not limited to ammonium sulfamate as the flameproofing material. It has been used in the specific examples for convenience, and because it is typical. The principles of selection and application of these flameproofing materials are disclosed in the Cupery patents, and in the interest of brevity this data is not repeated here.

The ammonium sulfamate contributes to the softening of the regenerated cellulose film to such an extent that it may be used in the absence of any other softener, if desired. Very satisfactory softening is obtained when this material is used together with a small amount of glycerol or related materials.

Preferably the sizing agents for the regenerated cellulose film softened with ammonium sulfamate, and related materials, are applied in the form of an emulsion of the hard wax and shellac. To maintain the stability of such emulsions in the aqueous softener baths to which they are added for application to the film, certain other materials, such as surface active agents, are added.

The invention is not limited to regenerated cellulose. The process described herein is also applicable to other smooth, non-fibrous, nonporous sheet material which, because of a high content of softener, flameproofing agent, etc., may have a tendency to stick to itself or other materials. It is particularly applicable to the water sensitive pellicles (films, webs, sheets, foils) cast from aqueous or aqueous alkaline cellulosic solutions or dispersions, for example, regenerated cellulose precipitated from viscose (solutions of cellulose xanthate), low (or lowly) substituted (not more than one mol of substitution per glucose unit, see U. S. A. Patent No. 2,123,883) cellulose ethers, low substituted cellulose esters and ether esters, including such specific materials of glycol cellulose, methyl cellulose, ethyl cellulose, cellulose glycolic acid and cellulose phthalic acid. The alkyl celluloses respond particularly well to this treatment.

In the preferred embodiment of this invention, the sizing or anti-stitcking agents are applied to transparent, regenerated cellulose sheet material while it is in the gel state, but it is to be understood that the sheet material may be dried and rewetted. This last procedure is generally to be avoided for economic reasons, since it necessitates an additional step in the manufacture, thus increasing the cost.

The gel regenerated cellulose sheet material in continuous form is ordinarily run through a bath containing the sizing in the desired concentration. This is most conveniently done just prior to the drying operation, and at the same time as the impregnation with the softener, flameproofing material, etc. Before entering the drier, the excess sizing together with the excess flameproofing solution, may be removed by suitable squeeze rollers, scraper rods, doctor knives, or the like. The amount of sizing which is applied is controlled either by adjusting the concentration of the sizing agent in the treating bath, or by regulating the amount of the excess removed.

If desired, the sheet material may be treated with a softener bath, the excess removed as described above, and then the solution or dispersion of the sizing agent applied by dip rolls, sprays, or the like. In some instances it may be desirable to produce sheet material containing no softener. In the interest of brevity, conventional specific details of sizing are not given in this application.

Preferably only very minute quantities of the sizing substances are applied to the transparent regenerated cellulose sheet material. The amount on the film after drying is usually less than 2% of the product, and may even be as little as a few hundredths of a per cent.

In the formation of the sizing emulsion, carnauba wax or an equivalent hard wax, such as candelilla wax, montan wax and stearamide, is an essential ingredient. Commercial availability has considerable influence upon the selection of this material.

Although various grades of shellac which are available can be used in this invention, the purified colorless forms are preferred where clear water-white finished sheet is desired.

As surface active agents, specific mention may be made of sulfonated aliphatic hydrocarbons, for example, sulfonated kerosene, and substituted sulfonated alkyl aryl hydrocarbons, for example, the mono-sulfonated alkyl benzenes in which the

alkyl radical whether straight or branched chain, contains 10 to 14 carbon atoms of mixtures of such alkyl benzenes in which the average alkyl radical carbon content is 12.5. The free acid or soluble salts (for example, sodium) may be used. Such products as the alkyl naphthalene sulfonic acids and water soluble salts of sulfuric esters of aliphatic alcohols containing at least 8 carbon atoms (more specifically, the sodium salts of sulfuric acid esters of normal primary aliphatic alcohols having 8 to 18 carbon atoms) may also be used.

As emulsifying agents, the soluble organic and inorganic soaps of such acids as stearic acid, oleic acid, and other long chain aliphatic acids, are suitable. Specific compounds of this type are sodium palmitate, triethanolamine oleate, and the like.

The nature of the foregoing ingredients and the technique of preparing the emulsions, are set forth in the specific examples.

In carrying out the sizing treatment, it is possible to so prepare the solution, control the quantity thereof applied, and dry the sized product, that it is not substantially inferior to an unsized product of the same material, as will be clear from the specific examples. This is particularly true so far as the retention of transparency and brilliancy.

The products of this invention resist cohesion, such as the caking of stacked sheets when stored under pressure and/or exposure to atmospheres of high humidity, as much as or more than similar unsized sheets, even though the product may contain more than twice the quantity of softening agent, flameproofing agent, etc., as the unsized product.

The freedom from sticking and caking is as fully satisfactory when ammonium sulfamate and the like is used as when only the commonly used glycerol (as a softening agent) is present.

A very practical feature of the process of this invention is that it may be carried out at practically no increase in cost, and without any alteration in the machine usually used for producing transparent regenerated cellulose sheets, and in the methods of subsequent handling used by the manufacturer, converter and consumer.

In résumé, it may be stated that the present invention enables the production of clear, transparent films which are not only highly flexible and durable under varying conditions of temperature and humidity, but which are also flame-resistant and highly resistant to sticking and caking together.

As many apparently widely different embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that this invention is not limited to the specific embodiments thereof except as defined in the appended claim.

I claim:

The process of producing flameproof, non-sticking, transparent, regenerated cellulose sheet which comprises passing gel regenerated cellulose in sheet form through an aqueous bath comprising 7% ammonium sulfamate, 1.5% glycerol, and sufficient emulsion of the composition:

	Parts
Carnauba wax	22.7
Stearic acid	9.7
Morpholine	11.3
Shellac (bleached)	18.2
Mono-sulfonated alkyl benzene	2.3
Water	391.0

to give 0.5% solids and thereafter drying said sheet material.

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CERTIFICATE OF CORRECTION.

Patent No. 2,316,496. April 13, 1943.

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It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 1, first column, line 46, for "reseach" read --research--; page 2, first column, line 48, for "0.5 solids" read --0.5% solids--; and second column, line 17, for "of" read --as--; line 22, for "anti-stitcking" read --anti-sticking--; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 15th day of June, A. D. 1943.

(Seal)

Henry Van Arsdale,
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