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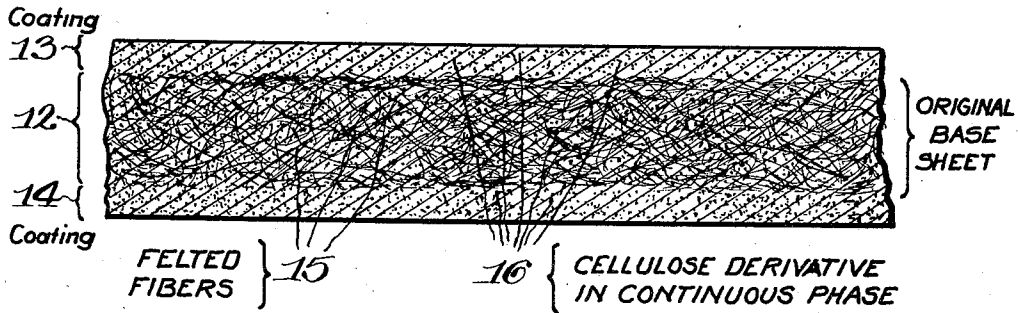
MANUFACTURE OF FELTED PROOFED FIBROUS MATERIAL

Filed Sept. 1, 1932



FELTED FIBERS, AND
RESIDUE OF HYDRATED
CELLULOSE } 10 11 { CELLULOSE DERIVATIVE
IN CONTINUOUS PHASE

Fig. 1



Coating 13 }
12 }
14 }
Coating
FELTED FIBERS } 15 16 { CELLULOSE DERIVATIVE
IN CONTINUOUS PHASE

Fig. 2

Witness:
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MANUFACTURE OF FELTED PROOFED
FIBROUS MATERIALS

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21 Claims. (Cl. 92—21)

This invention relates to the manufacture of sheets containing fibrous materials and cellulose derivatives soluble in organic solvents but insoluble in water.

An object of this invention is to prepare a material that is highly resistant to penetration of oils, greases, fats, waxes and the like. A still further object is to prepare a material that retains its strength when in contact with water, and is at the same time highly waterproof and resistant to the penetration of water vapor. Another object of this invention is to prepare a material that is highly translucent or transparent, and at the same time strong and flexible.

A particular object of our invention is to prepare a sheet containing hydrated cellulose fibers, a soluble cellulose derivative and a plasticizer thoroughly disseminated throughout the mass, and at the same time to provide a sheet that is highly translucent or even transparent.

A still further object of the invention is to provide a sheet having a body or central portion containing fibers, a soluble cellulose derivative and a plasticizer thoroughly disseminated throughout the fibers, and one or more surfaces of plasticized soluble cellulose derivative, which surface is an integral part of the composite sheet, being intimately united with the soluble cellulose derivative in the body or central portion of the sheet.

Another particular object is to provide a sheet-like structure the body of which is composed of a fibrous material having a soluble cellulose material and a plasticizer therefor thoroughly dispersed therein, a surface coating of a soluble cellulose derivative, and modifying agents intimately united with the soluble cellulose derivative and plasticizers of the interior structure, said surface being of such a nature as to be highly resistant to the transference of oils, fats, greases, water and the water vapor, oxygen, etc.

A specific object is to provide a sheet, the interior of which is composed of cellulose fibers, nitro cellulose and a plasticizer therefor, and a "water-vapor proofing" material, at least one surface of the sheet having a base of nitrocellulose and a plasticizer.

Other and ancillary, objects and advantages, and uses will appear in or be obvious from the following description and the appended claims.

For wrapping many articles it is highly desirable that the wrapping material be both water and grease proof. Glassine paper is highly grease and oil proof but has very poor water resistance. Papers, when waxed, as for example with paraffin, have water resistance, but many

greases soften the wax. Furthermore, the wax cracks on the folds, and such waxed paper is therefore unsatisfactory for many purposes. Regenerated cellulose, as found for example in viscose sheets, is grease-proof but has poor water resistance and low wet strength. Where resistance to water and water-vapor is to be obtained, products have been made of regenerated cellulose coated with a cellulose nitrate base lacquer, as for example, the product described by Charch and Prindle in their U. S. Patent No. 1,737,187, of November 26, 1929. Such a product, while resistant to the transference of water vapor, is unsatisfactory for use in contact with wet materials and liquid water because the same cause the material to delaminate, weaken in strength, and lose its water resistance and other valuable properties. Furthermore, such products are very brittle at low temperatures making them unsatisfactory for use where low temperatures are encountered, such for example, as is described in U. S. patent to Birdseye, No. 1,773,079, August 12, 1930, on the freezing of foods in packaged form.

According to the present invention the fibrous body may be readily coated with numerous agents without disadvantage, because the fibers of the base are encased in a continuous filling film which protects the fibers from injury or change in physical form by water or the like, and which is suitable for integral union with the coating material.

In carrying out this invention, any animal, vegetable or mineral fibers may be used which are capable of being felted, such a hair, wool, cotton, asbestos, grass, jute, mechanical or chemical wood pulp and the like. Cellulose fibers are preferred because of the varieties which are available, and because of the valuable characteristics which can be utilized in the preferred form of this invention. In further detailed description, chemical wood pulp is specifically meant when the term pulp is employed, but in general many of the statements made regarding it are applicable to any fibrous pulp which may be used.

In carrying out our invention we employ as a base a composition comprising a fibrous material, such as cellulose, a cellulose derivative that is soluble in organic solvents but insoluble in water, and an agent to increase the flexibility of the cellulose derivative. We may also employ agents to render the material more resistant to permeation by water or water vapor, and we may also employ other modifying agents such as resins and coloring agents, as for example, dyes or pigments.

In many cases, and for special purposes, we prefer to apply a coating over the base sheet. Where such coating materials are used, we prefer to use a material having as a base a cellulose derivative insoluble in water, but soluble in organic solvents which are capable of also dissolving the cellulose derivative contained in the base sheet. For example, where the base sheet contains cellulose nitrate, we prefer to employ a lacquer having a cellulose ester base as a coating material, dissolved in solvents which will also dissolve the cellulose nitrate in the base material. In such coatings we also employ a material to render the cellulose ester more flexible and elastic. In one valuable embodiment of our invention we also employ a resin or gum, either natural or synthetic, such as ester gum or a chlorinated diphenyl resin, and an agent to render the material more resistant to the penetration of water vapor, as for example, stearic acid.

The exact proportions of the various ingredients will vary according to the qualities desired in the finished product, and the use to which the product is to be put. The following more detailed descriptions illustrate several ways of obtaining a material having desirable properties described above. It will be apparent, however, that wide variations are possible in the choice of materials, in the proportions used and in the manner in which they are combined.

A paper-forming stock may be made of water, cellulosic pulp and a cellulose derivative soluble in organic solvents with or without modifying agents. Such a mixture may be beaten, as in preparation for paper formation on a Fourdrinier or cylinder paper machine. The stock may be beaten to any predetermined freeness, indicating an extent of hydration; it may be partially hydrated or it may be highly hydrated. There is no difficulty in felting stock of cellulose fibers and nitrated wood cellulose fibers, or other fibrous cellulose derivative, whatever the proportion of the two fibers up to practically 100% of nitrocellulose fibers. Such proportion is however inordinately beyond the requirements for the preferred usages of the invention. At 70% nitrocellulose fibers and 30% cellulose fibers, the resulting felted sheet has an appearance of an ordinary sheet of paper. At 10% nitrocellulose fibers and 90% cellulose fibers the resulting felted sheet has all of the essential characteristics of a sheet made out of 100% of that same cellulose fibers.

Where the base material is to be used directly, we prefer a hydrated cellulose in combination with, for example, cellulose nitrate, or cellulose acetate, and a plasticizer for the cellulose ester with or without other modifying agents. The hydrated cellulose, such as hydrated chemical wood pulp is especially useful where a high resistance to organic solvents, to oils, fats, greases, etc., is to be obtained. A highly hydrated cellulose is also desirable where a high degree of transparency or translucency is desired, and we have found that highly transparent and translucent sheets may be made from mixtures of hydrated cellulose and nitrocellulose. The degree of hydration of cellulose affects its freeness, so that a highly-hydrated cellulose has a low freeness, and consequently must be run slowly on a paper machine, resulting in a low per diem production. We have found that by the addition of a cellulose derivative, such as cellulose nitrate fibers, to this hydrated stock, the freeness is greatly increased, so that we may either increase the speed of the paper machine for a cellulose of a given hydra-

tion or use a more highly hydrated cellulose at a given speed.

We have discovered that sheets of hydrated cellulose of the glassine type, which are known to resist penetration by fats, are also impermeable to organic solvents for cellulose esters and ethers. We have also found that small quantities of such esters or ethers in such sheets of hydrated cellulose do not render the sheet permeable to such solvents. Not until a substantially large proportion of such esters or ethers are present does such a sheet become permeable to such solvents. We have discovered that in order to secure penetrability by such solvents it is necessary to increase the proportion of soluble fibers, or to decrease the degree of hydration, or to do both. It is not practical, therefore, to make a paper like sheet of say 95 parts of a wood cellulose hydrated to a freeness of 120 (Green) and 5 parts of nitrocellulose, and then to wet the sheet with nitrocellulose solvents, as for example, ethyl or butyl acetate, in order to dissolve the particles of nitrocellulose and cause them to coalesce. The hydrated cellulose prevents the nitrocellulose solvents from penetrating the sheet so that even after five or ten minutes in contact with dry solvents, the nitrocellulose fibers in the interior of the sheet retain their fibrous form.

We are aware that it is old to mix fibrous material such as wood pulp or rag stock, asbestos, leather fibers, etc., with a cellulose ester or ether, and then form the mixture into a sheet. It is also old to wet a sheet so formed with an organic solvent capable of dissolving the cellulose ester or ether and causing it to coalesce and form a more or less continuous film. Such processes as have been described, however, are not applicable to a sheet made of cellulose that has been hydrated to the point where it is resistant to the penetration of oils, fats, greases, etc., for the reasons already pointed out.

In order to increase the penetrability of such a sheet to the usual non-aqueous solvents, it is necessary either to increase the proportion of nitrocellulose, or to decrease the degree of hydration. For example, when a stock containing 20% nitrocellulose fibers and 80% hydrated (freeness 120 Green) cellulose fibers is felted, the resulting sheet is easily penetrated by a non-hydrous solvent for nitrocellulose, whereas a sheet from stock containing 5% nitrocellulose fibers and 95% of similarly hydrated cellulose fibers is, in a practical sense, impervious to such a solvent. The following is a typical solvent for such a comparison:

	Percent
Ethyl acetate	40
Butyl acetate	10
Toluol	35
Castor oil	10
Tricresyl phosphate	5

For a given proportion of cellulose derivative there is a limiting degree of hydration when a specific solvent is to be applied for solution of the cellulose derivative. The limiting factors may be readily determined by experimentation with the specific materials, and other conditions, such as time and temperature.

When one or more soluble modifying agents as for example, plasticizing agents, resins, etc., for the cellulose derivative are present in the paper forming stock with the cellulose derivative, either separately, or wholly or partly associated with it, there is less need for considering the degree of

hydration. The original composition may be such that no solvent need be applied, and heat treatment of the paper, as during drying, or during hot calendering, will effect distribution.

Thus we have discovered a method of coalescing soluble matter in a sheet of hydrated cellulose.

We found for example that a stock made from 90% of a wood cellulose hydrated to a freeness of 120 (Green), and 10% of nitrocellulose, was extremely difficult to wet with a solvent composed of

	Percent
Ethyl acetate-----	40
Butyl acetate-----	10
Toluol-----	35
Castor oil-----	10
Tricresyl phosphate-----	5

whereas a sheet made from 80% of a similar hydrated cellulose and 20% cellulose nitrate was quite easy to wet with the above solvent.

Where we use a hydrated cellulose, a cellulose ester and a plasticizer for the cellulose ester, we have been able to obtain as by hot calendering, a sheet having a high degree of transparency, which is also much more flexible and stronger than, for example, glassine paper. A sheet made by this process retains its strength under water to a surprising degree, and is substantially water proof. It also is more highly resistant to penetration by water vapor than ordinary glassine paper.

Another manner of obtaining our desired product is to make use of a plasticizer which may be added at the beater, which is a solvent for the cellulose ester, and then pass the sheet between heated rollers under high pressure, preferably as in a paper calender or super calender, whereupon the particles of cellulose ester and plasticizer coalesce and embed the hydrated cellulose, filling up interstices of the paper. In this process it is not necessary to use a volatile organic solvent to dissolve the cellulose ester, although it may sometimes be desirable to do so.

To secure a high degree of moisture and grease proofness, flexibility, and transparency, we prefer to employ, for each 100 parts by weight (dry weight of cellulose) of hydrated cellulose, at least 6 parts of nitrocellulose and a suitable amount of plasticizer depending upon the results desired. These may be mixed in a paper beater until substantially all of the plasticizer has been taken up by the stock, and then run on the paper machine. Surprisingly enough, we have found that the addition of the nitrocellulose and the plasticizer to the hydrated stock does not slow up the rate at which it may be run on the paper making machine. After drying in the usual paper mill drier, such a paper is highly translucent, flexible and waterproof. Our preferred process, however, contemplates treating the sheet formed as described above by an ironing process, as in a paper calendering or super calendering machine. The calendering treatment causes the nitrocellulose to dissolve in the solvent plasticizer and to coalesce, and at the same time further increases the transparency of the hydrated cellulose, thus producing a highly transparent and glazed sheet, that is highly resistant to water, grease, fats and oils, and which is highly resistant to water vapor and to oxygen and other gases.

In order that the invention may be made clear, the following examples are given by way of illustration. It is, of course, to be understood that the examples are not to be taken as limiting the scope of the invention, since they are given mere-

ly by way of illustrating how some of the details of the process may be carried out.

Example I

900 lb. of bleached chemical wood pulp (dry weight) is placed in a paper beater and beaten to a freeness of 120 (Green). 100 lb. of nitrocellulose is then added and the hydrated pulp and nitrocellulose are mixed in the beater until the nitrocellulose is thoroughly mixed into the pulp. 25 lb. of dibutyl phthalate and 70 lb. of castor oil are then added, and mixing in the beater continued until substantially all of the dibutyl phthalate and castor oil has been taken up on the fibers.

The beater is then discharged into the chest and water added. The stock is then run through Jordan machines, and made into paper furnish by adding additional water if necessary to produce the proper weight of paper. Ordinary paper makers' practice is followed, bearing in mind increased freeness due to the nitrocellulose.

The paper is made on any suitable paper making machine in the usual manner. The paper so made is somewhat translucent, and is water repellent. In order to secure the full benefit of the nitrocellulose and plasticizer we prefer to subject the paper to an ironing process. For this purpose, heated calender rolls are satisfactory. The paper as made above is therefore run through calender rolls, or preferably through a super calender, the rolls of which are heated to a temperature of not less than 175° F.

Example II

700 lb. of bleached chemical wood pulp (dry weight) is placed in a beater and beaten to a freeness of 100 (Green); 300 lb. of cellulose nitrate is then added and the hydrated cellulose and nitrocellulose are thoroughly mixed.

The above stock is made into sheets in the same manner as described in Example I, or by any ordinary paper making procedure. We have found that where a hydrated wood pulp cellulose is used, nitrocellulose prepared from wood pulp cellulose, such as that made according to the process described in the U. S. patents of Wm. Courtney Wilson, No. 1,883,215 of October 18, 1932, and No. 1,925,162 of September 5, 1933, is especially useful for our purpose, because the fibers of nitrocellulose are of dimensions similar to the dimensions of the wood pulp, and also because its loose fluffy condition makes it easy to mix with the paper stock and become more evenly dispersed in the paper. It is also advantageous because the nitrated wood cellulose fibers have a relatively small diameter as compared, say, to nitrocellulose made from cotton linters, so that it dissolves more rapidly in solvents and in solvent plasticizers. Its physical identity makes it less detectable as a foreign fiber in paper stock, and its small size limits the spacing between the cellulose fibers.

Where the sheet of mixed insoluble fibers and soluble inclusions is to be coated with a cellulose ester or ether base solution, a wider choice of specific base materials is possible. Our invention, therefore, contemplates broadly the use of any fibrous materials having dispersed therein a cellulose ester or ether soluble in the solvents employed for the coating solution, when coated with a coating material such as is hereinafter described. We may use, for example, mixtures of cellulose ester or ether with such fibrous mate-

rials as wood pulp cellulose, wool, leather fibers, asbestos and like fibrous materials.

For the sake of clarity the following description is confined to fibers of wood pulp cellulose and cellulose nitrate which are our preferred materials for most purposes. It is to be clearly understood, however, that wherein the term wood pulp, or wood pulp cellulose appears in the following description, that other fibrous materials such as cotton cellulose or rag stock, wool fibers, asbestos fibers and other fibrous materials may be substituted wholly or in part. It is also to be understood that where the term cellulose nitrate or nitrocellulose appears in the following description, other soluble esters or ethers of cellulose may be used either alone or as mixtures without departing from this invention.

In carrying out our invention as applied to a composite sheet, coated on one or both sides, we first make up a sheet consisting of wood pulp cellulose having cellulose nitrate dispersed therein. A satisfactory method of securing such a sheet is to place the wood pulp and the cellulose nitrate in a paper beater and operate the beater either as a beater or a mixer until a uniform mixture is secured. We may also at this time add other materials in the beater, such as sizing agents, coloring matter such as dyes and/or pigments, agents for plasticizing the nitrocellulose, fillers, and the like. After thorough mixing, the stock is formed into a sheet, as for example, on a paper making machine, or, where sheets having a considerable thickness are desired, on a multiple cylinder machine. In forming the sheets on such machines, most of the water is removed, and in most instances the sheet may be handled in a manner similar to the handling of ordinary paper pulp products.

Wide variations in the proportions of wood pulp and cellulose nitrate are possible, and the proportions may be varied according to the product desired. In some cases, where it is merely desired to secure good adherence between the base sheet and the coating, as little as 5 or 10 per cent of nitrocellulose may be used. On the other hand, where a highly water proof material is desired, a larger amount, say from 15% to 40% of nitrocellulose is to be preferred. In still other cases, where flexibility, transparency, or other special properties are desired, the nitrocellulose may predominate, and as much as 85% or 90% of nitrocellulose may be used advantageously.

The type of fibrous material selected, will be determined by the requirements of the product. Where a high tensile strength is desired, a long fiber such as kraft pulp, wood fiber cooked by a neutral sodium sulfite process, or flax fiber may be used. Where transparency is desired, a hydrated cellulose such as described in Examples I and II is useful in our process and these examples may be considered as one suitable form of base sheet. Where heat resistance is desired, asbestos fibers in combination with a cellulose ether such as ethyl cellulose gives a desirable base. After a proper base sheet such as described above has been prepared, we apply a coating on one or both sides of the sheet. We are able to secure perfect adherence between the base and the coating by employing solvents for the coating material that are also solvents for the cellulose ester or ether in the base sheet. For example, if the base sheet contains cellulose nitrate, we may use as a coating material cellulose nitrate and a plasticizer dissolved in a suitable solvent such as described in some following exam-

ples. If the base sheet contains cellulose acetate, we may use cellulose acetate and a plasticizer dissolved in a solvent such as is described in some following examples, which solvent is capable of dissolving the cellulose acetate contained in the base sheet. We also contemplate using in the coating cellulose esters or ethers which are different from the cellulose ester or ether contained in the base sheet, provided the solvent used for the coating material is capable of dissolving the cellulose ester or ether used in the base sheet. Thus we may use cellulose nitrate in the base sheet, and a coating material containing cellulose acetate and a plasticizer dissolved in a solvent also capable of dissolving the cellulose nitrate used in the base sheet. We thus secure a structure wherein the surface area is continuous and microscopically homogeneous, and is integral and continuous with the continuous phase of the base sheet.

In order to illustrate the product of the present invention a representative drawing is made of exemplary embodiments of the invention.

Fig. 1 illustrates a felted fibrous sheet in which the soluble cellulose derivative, originally present during felting as discrete units, is coalesced into an integral body as a continuous phase in the sheet.

Fig. 2 is a sheet similar to that of Fig. 1, in which a coating film on the two surfaces is integrally united to the continuous phase, having therefore two surface films integrally united to each other by a continuous bond through the sheet.

Referring to Fig. 1, the numeral 10 designates felted fibers. These may be any fibers as described and in particular may be cellulosic fibers which in the paper forming stock had been highly hydrated. Thus they are united to each other by the dried residue of hydrated cellulose. Should these fibers be other than hydrated cellulose, to which the latter substance has been added in the paper forming stock, substantially the same condition will obtain. The numeral 11 designates the continuous phase which houses the fibers comprising as a base a soluble cellulose derivative, with or without modifying agents, added either in the paper furnish, or thereafter to the felted sheet.

The paper sheet of Fig. 1 contains material soluble in organic solvents. Using such a sheet in character which is penetrable by a suitable solvent, a coating may be applied which can be anchored to and integrally united with the continuous phase 11 of the sheet.

Fig. 2 represents such a product formed from a structure like that of Fig. 1. Although both surfaces are coated, the coating of one surface only is contemplated. In Fig. 2 there is a body portion 12, a surface portion 13, and a second surface portion 14. The body portion contains felted fibers 15, and a continuous phase of coalesced cellulose derivative 16, as described for Fig. 1. The surface layers may be the same or different in composition, but each comprises essentially a base material capable of application for integral union with the material 16. Cellulose esters and ethers are suitable. It is preferred that the bases of material 16 and of a surface layer be the same, such as nitrocellulose, or cellulose acetate. The surface layers may be modified, as by plasticizers, colored, or decorated, as elsewhere described.

A structure such as that of Fig. 2 is free from the danger of delaminating, and the fibers within

are protected by the integral continuous material which runs from surface to surface.

Our preferred coating is most conveniently applied from a solution, but we may also apply it as a sheet, by wetting the base sheet and/or the coating sheet with a solvent capable of dissolving both the coating sheet and the cellulose ester or ether in the base sheet, and pressing the two sheets together.

Our preferred coating material consists essentially of a solution of cellulose ester or ether in a solvent capable of dissolving the cellulose ester or ether in the base material. In most cases it is desirable to have present also a plasticizer for the cellulose ester or ether employed, to increase the flexibility and elasticity of the coating. Such plasticizers are well known in the art. For example, suitable plasticizers for cellulose nitrate are dibutyl phthalate, tricresyl phosphate, castor oil, and certain balsam-like resinous materials. Suitable plasticizers for cellulose acetates are tricresyl or triphenyl phosphate, toluene sulfonamid and some of its derivatives, and other material known to increase the elasticity and flexibility of cellulose acetate films. Many of the agents named above are also desirable for use with such cellulose ethers, such as ethyl, butyl, amyl and benzyl celluloses.

For many purposes it is desirable to use a resin, either natural or synthetic in the coating material. Examples of such resins are, damar, shellac, ester gum, glycerol-phthalic-acid resins, phenol formaldehyde condensation products, vinyl resins, etc. The resin selected should be compatible with the cellulose ester or ether employed, that is, upon evaporation of the solvent, the film should have the appearance of being homogeneous.

We may also use coloring materials such as pigments or dyes, either in solution or in suspension in the coating material, to produce color effects. For some purposes metal powders such as the well known bronze or aluminum powders may be used. Furthermore, we may add to the coating solution a soluble material which, upon evaporation of the solvents, crystallizes out in the coating layer to form crystalline designs, such as are obtained by the crystallizing lacquers. Phthalic acid is useful in a nitrocellulose base coating for crystallizing effects.

Where water proofness, and especially water vapor proofness is important, we may use a coating material designed to increase the moisture proofness of the base sheet. For example, we may add to the coating compositions such materials as fatty acids having more than 12 carbon atoms as for example, palmitic and stearic acids. We may also employ for the same purposes, various waxes or waxy materials such as spermacetti wax, or paraffin wax, and other materials known to aid in preventing the penetration of water vapor.

The following examples of suitable coating compositions are given merely by way of illustration, and are not to be considered as limiting the broader aspects of the invention.

Example III

	Parts by weight
Nitrocellulose	100
Castor oil	60
Dibutyl phthalate	40
Toluol	360
Alcohol	40
Butyl acetate	250
Ethyl acetate	150

This coating solution is suitable for use where a high degree of flexibility is desired. It is substantially unaffected by water, but is not water vapor proof. The solvents in a composition as given above will dissolve cellulose nitrate in the base sheet, and cause it to blend with the nitrocellulose, resulting in an integral substance extending as a continuous phase throughout the sheet.

Example IV

	Parts by weight
Nitrocellulose	30
Tricresyl phosphate	21
Ester gum	11
Toluol	153
Alcohol (ethyl)	60
Ethyl acetate	100
Butyl acetate	25

This produces a coating that is highly resistant to water.

Example V

	Parts by weight
Nitrocellulose	30
Castor oil	21
Resin	11
Stearic acid	10
Solvent	340

The resin may be any resin compatible with nitrocellulose, such as ester gum, phthalic acid-glycerol resins, damar, shellac, etc. The solvent may be any solvent or mixture of solvents capable of holding the non-volatile ingredients in solution until substantially all the solvent has evaporated, such for example, as the solvent mixture given in Example IV. The above lacquer is highly resistant to the penetration of water and water vapor.

Example VI

	Parts by weight
Cellulose acetate	165
Toluene ethyl sulfonamid	175
Acetone	212
Methyl ether of ethylene glycol	500
Alcohol (ethyl)	200

The solvent given in this example is capable of dissolving not only acetone soluble types of cellulose acetate, but will also dissolve cellulose nitrate and most of the cellulose ethers. It is useful, therefore, in combining a cellulose acetate surface layer to a base sheet having a cellulose acetate, cellulose nitrate or cellulose ether therein. The solvent may be used with cellulose nitrate or the cellulose ethers for applying cellulose nitrate or cellulose ethers as a coating to base sheets having a cellulose acetate therein.

Example VII

	Parts by weight
Ethyl cellulose	100
Tricresyl phosphate	25
Spermacetti wax	25
Resin	15
Solvent	700

The solvent should be chosen that is capable not only of holding the ethyl cellulose and other non-volatile ingredients in solution, but which is also capable of dissolving the soluble cellulose derivatives forming the soluble cellulose derivative in the base sheet, so that an intimate union is formed between the cellulose ether containing surface and the continuous phase of the base sheet.

Although we prefer soluble fibers to facilitate

formation of the sheet, it is to be observed that in the finished sheet the soluble fibers are coalesced into a continuous phase. Hence, for some uses of the invention it is immaterial whether the continuous phase is derived from fibers or from other forms of the soluble component.

The product obtained by felting fibers, hydrated cellulose, and soluble cellulose derivatives, preferably in fibrous form, is a useful embodiment of the invention without a treatment to coalesce the soluble material. As stated, such a sheet containing hydrated cellulose has desirable resistant properties, like glassine paper. The soluble material therein serves to increase the normally low freeness of the furnish. In the finished product such material may be coalesced to a degree at the surface when a solvent, as in an applied lacquer coating, is used to wet the surface. Thus it serves to anchor the felted sheet, either to a coating or to any surface which is wet with a suitable solvent.

Inasmuch as products embodying the present invention are contemplated for extensive use in substitution for papers or sheets now known, it is in the interest of economy and low cost to reduce to a minimum the amount of soluble cellulose derivative. Every endeavor is made, therefore, for any special use, to secure the desired properties with as low a content of the more expensive ingredients. It is therefore contemplated that for special uses there may be departures from the specific illustrations herein given, with respect to the ingredients required, the proportion, and the treatment in process. Anyone skilled in the art may do this after fully comprehending the exemplary disclosures here made.

Whatever the fibers are which form the body of the material we have found that the presence of hydrated cellulose in the paper forming stock has a profound effect upon the character of sheet which results. It is well known that this may be produced by mechanical action on cellulosic fibers in water, forming a gelatinous film of hydrated cellulose on the fibers, or even converting the fibers almost entirely into a gelatinous mass. In our preferred usage of chemical wood pulp, we may hydrate the fibers, retaining fibrous characteristics, but it is to be understood that we may use other fibers and add to the stock a hydrated cellulose in gelatinous or in fibrous form.

The product like Fig. 1 may be used for wrappings as on food, packages, wall paper, linings, paper dishes, as a parchment substitute, lamp shades, as a receiver for a finishing coat.

The product like Fig. 2 may be used for substantially all the uses above given and may have many special uses, such as where a highly finished and glossy surface is desired, or where moisture-proofness is required. It is understood that either one or both sides may be finished with coating material, and the utility for special purposes thus regulated as desired.

Many other modifications and different embodiments of the invention will be found useful in numerous arts and in numerous combinations. In the appended claims we aim to define the invention as including all the forms herein described and suggested and all such departures and modifications of the process and the product which fall within the scope of the invention as defined by the claims.

Matter disclosed herein is described and claimed in a subsequent application Serial No. 3,032, filed January 23, 1935, as a continuation

in part of this application in response to a requirement for division.

We claim:

1. The method of making a paper-like sheet which comprises hydrating cellulose, felting into sheet form a paper-forming stock of said hydrated cellulose and fibrous material and a finely divided cellulose derivative, and drying said sheet.

2. The method of making a paper-like sheet which comprises hydrating cellulose to form hydrated cellulose, felting into sheet form a paper-forming stock containing said hydrated cellulose, fibrous material, a finely divided cellulose derivative, and a plasticizer therefor, and thereafter coalescing the cellulose derivative into a continuous phase in the resulting sheet.

3. The method of making a paper-like sheet which comprises hydrating cellulose, felting into sheet form a paper-forming stock of said hydrated cellulose and fibrous material and a finely divided cellulose derivative, and thereafter coalescing the cellulose derivative into a continuous phase in the resulting sheet.

4. The method of making a paper-like sheet which comprises hydrating cellulosic fibers to form a slow-stock, felting into a sheet said stock and a finely divided cellulose derivative, and thereafter coalescing the cellulose derivative into a continuous phase in the resulting sheet.

5. The method of making a paper-like sheet which comprises hydrating cellulosic fibers to form a slow-stock, felting into a sheet said stock and a fibrous cellulose derivative, and thereafter coalescing the cellulose derivative into a continuous phase in the resulting sheet.

6. The method of making a paper-like sheet which comprises hydrating cellulosic fibers to form a slow-stock, felting into a sheet said stock containing a finely divided cellulose derivative and a plasticizer therefor, and thereafter coalescing the derivative and plasticizer into a continuous phase in the resulting sheet.

7. The method of making a paper-like sheet which comprises hydrating cellulosic fibers to form a slow-stock, felting into a sheet said stock containing a fibrous cellulose derivative and a plasticizer therefor, and thereafter coalescing the derivative and plasticizer into a continuous phase in the resulting sheet.

8. The method of making a paper-like sheet which comprises hydrating cellulosic fibers to form a slow-stock, felting into a sheet said stock containing nitrocellulose in fibrous form, and thereafter coalescing the nitrocellulose into a continuous phase in the resulting sheet.

9. The method of making a paper-like sheet which comprises hydrating chemical wood pulp to form a slow-stock, felting into a sheet said stock containing nitrated wood pulp fibers, and thereafter coalescing the nitrocellulose into a continuous phase in the resulting sheet.

10. The method of making a paper-like sheet which comprises hydrating cellulosic fibers to form a slow-stock, felting into a dried sheet said stock containing a quantity of finely divided cellulose derivative capable of forming a sheet permeable to an organic solvent for said derivative, and applying such a solvent to the sheet for coalescing the derivative into a continuous phase in said sheet.

11. The method of making a paper-like sheet which comprises hydrating cellulosic fibers to form a slow-stock, felting into a dried sheet said stock containing a quantity of finely divided cel-

lulose derivative capable of forming a sheet permeable to a volatile organic solvent for said derivative, applying a mixture of such a solvent containing a plasticizer for said derivative, whereby to distend the derivative in the sheet, and evaporating the solvent.

12. A dried felted sheet comprising felted fibers, the dried residue of hydrated cellulose, and a finely divided cellulose derivative.

13. A dried felted sheet comprising felted fibers, the dried residue of hydrated cellulose, and fibrous cellulose derivative.

14. A dried felted sheet comprising the dried residue of felted highly hydrated cellulosic fibers, and finely divided cellulose derivative.

15. A dried felted sheet comprising the dried residue of felted highly hydrated cellulosic fibers and finely divided nitrocellulose.

16. A dried felted sheet comprising the dried residue of felted highly hydrated cellulosic fibers and nitrated cellulose fibers.

17. A dried felted sheet comprising the dried residue of hydrated cellulose, felted fibers, and a cellulose derivative extending throughout the sheet as a continuous phase in said sheet.

18. A dried felted sheet comprising the dried residue of hydrated cellulose, felted fibers, and a plasticized cellulose derivative extending throughout the sheet as a continuous phase in said sheet.

19. The method of making a paper-like sheet which comprises hydrating cellulose until it is capable of forming with fibers a grease-proof sheet, felting into sheet form a paper-forming stock containing said hydrated cellulose and finely divided cellulose derivative, and drying said sheet.

20. The method of making a paper-like sheet of grease-proof character which comprises hydrating cellulose until it is capable of forming with fibers a fibrous grease-proof sheet, felting into sheet form a paper-making stock containing: said hydrated cellulose, finely divided cellulose derivative, and a resinous modifying agent.

21. A fibrous sheet comprising felted fibers, the residue of hydrated cellulose, and a continuous phase of modified cellulose derivative containing said fibers, said modified derivative containing a resinous modifying agent.

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