

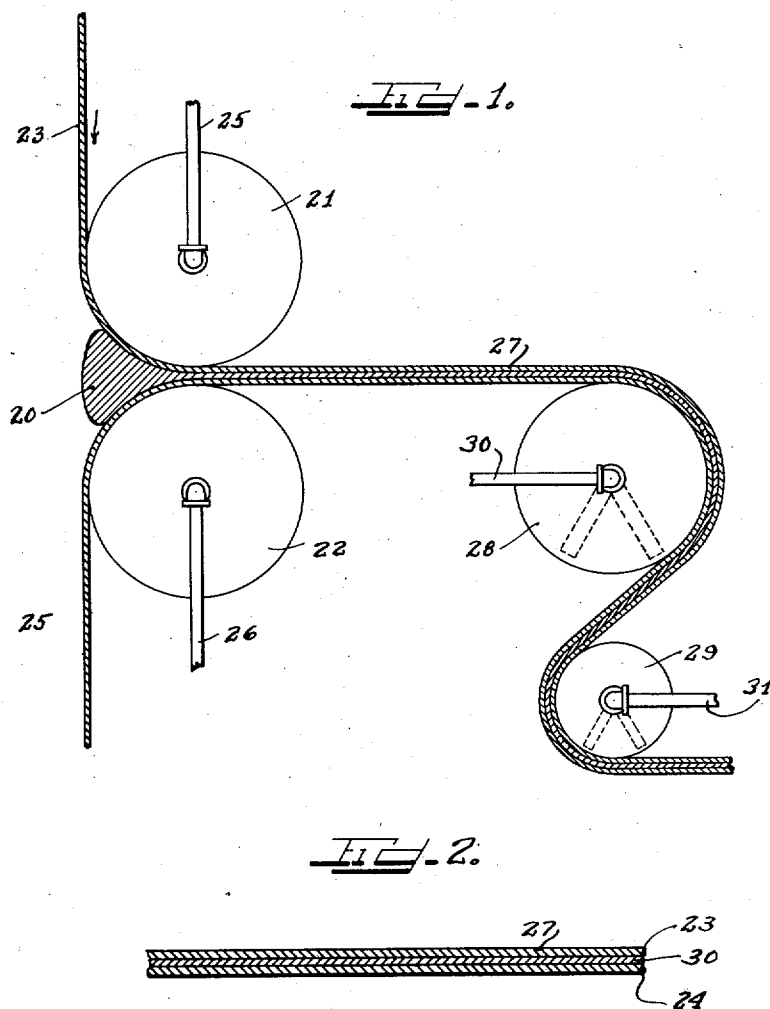
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LAMINATED SHEET MATERIAL

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LAMINATED SHEET MATERIAL

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This invention relates to laminated sheet material and particularly to a moistureproof, water-proof and gasproof flexible sheet material suitable for wrapping purposes.

5 This application constitutes a continuation in part of copending application entitled "Coated sheet material", Serial No. 693,741, filed October 16, 1933.

Because of the greatly increased use of pack-
10 aging materials for foodstuffs, tobacco and the like, there has developed a need for papers having particular properties. For example, moistureproofness (or the ability to withstand the passage of water vapor) has become a very im-
15 portant factor since it is often desired either to keep moisture in a package or to exclude it from the contents of a package. For this purpose waxed papers have been used heretofore. How-
20 ever, such papers suffer from the objection that they may block or stick together during warm weather. Moreover when containers wrapped with such papers are allowed to stand in stores and homes they have a tendency to collect dust and dirt thereby becoming unsightly. Further-
25 more although waxed papers may be self-sealed to form a tight package, the sealing bond is weak.

As a result there is a need today for a sheet or web material which can be printed, glued,
30 creased and otherwise handled like an ordinary sheet of paper on standard converting machines; which will be free of color and odor; and yet which will be highly moistureproof.

After much experimentation we have produced
35 laminated papers which offer a satisfactory solution for the aforementioned requirements. In accomplishing this we make use of a composition which is applied between the two webs without changing the characteristics of the outer sur-
40 faces of the webs. Moreover sheets of different characteristics may be combined to produce special effects. Thus, it may be desired to have a good printing surface on one side and a highly greaseproof surface on the other and the whole
45 combination to be moistureproof. This would result in a combined sheet capable of withstanding the passage of moisture, grease and gas (or flavor as from products containing essential oils).

Up to the present time laminated papers which
50 are available do not satisfactorily fulfill these

conditions. Thus, for example, papers laminated with asphalt will have a dark color and may have an odor. Moreover a relatively large amount of asphalt must be used to secure a satisfactory moistureproofness in the paper. In
5 cases where an oily or greasy material is placed in contact with the paper there is danger of the dark colored asphalt bleeding and staining the paper.

For these reasons the use of moistureproof
10 laminated paper has been restricted to fields where the foregoing objections are of no consequence. There is, however, a large field which has not yet been properly satisfied, requiring the use of a light colored, odor-free, printable, glue-
15 able, moistureproof sheet and it is this field to which the present invention relates. Thus the tight wrapping of packages has become of great commercial importance but up to the present
20 time a satisfactory sheet has not been developed which can be used on the machines now in use. Other important uses of our laminated papers are also contemplated by our invention as for envelopes or wrappers to contain foods or other
25 substances.

We are aware that laminated papers have been made by the use of paraffin, or similar waxes, only. However, the product thus obtained has certain distinct limitations which restrict its use-
30 fulness accordingly.

Thus the wax itself is of such low viscosity at the temperature of application that it will strike into the papers unless they are very dense and non-porous, as, for example, glassine or trans-
35 parent cellulose film. On account of this penetrating property, more wax will be absorbed than is necessary for the laminating bond. This not only adds to the cost of the laminated paper but also increases its weight without materially im-
40 proving the moistureproofness. In certain papers the penetration is undesirable since it tends to darken the color of the sheet, interferes with the printing surface of the paper and makes it so water repellent that the ordinary glues or ad-
45 hesives will not join the surfaces together. The latter property is particularly undesirable where the sheet is used as a wrapper to be glued around packages.

Another serious objection is that wax alone makes a weak bond so that laminated papers thus
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prepared may be separated readily into their component layers. This is true whether the papers are of the unhydrated or the hydrated type, such as glassine.

Again, wax alone is relatively brittle and inflexible so that the creasing of wax-laminated papers tends to break down the structure of the binding layer and thereby impairs the moistureproofness. This is of great importance in the application of papers to packages and the like, whereby they are subject to folding and creasing.

Furthermore, it is not feasible to incorporate pigments and the like satisfactorily with wax only, since they do not remain in suspension and, therefore, will not add to the whiteness or opacity of the laminated paper made therewith.

In Johnson U. S. Patent 229,045, June 22, 1880, there is reference to a paper produced by laminating two unsized papers using a thin mixture of caoutchouc with either paraffin or Japan wax. However, it is apparent that this product is entirely different from ours in that a thin composition of this type would strike into the papers and impregnate the fibres of the papers so that the resultant product would be water repellent on the outer surfaces. As a consequence the sheet would be darkened in color, could not be printed or glued satisfactorily. Moreover a composition of this sort would make such a weak bond that the two sheets of paper could be separated readily. For the same reason the laminating material would not form a continuous film and our work has shown this to be a prime requisite for obtaining good moistureproofness.

However, we have found that our compositions, which have a high viscosity, are so cohesive that plies united therewith can only be separated with difficulty or not at all. Our compositions will not strike through the paper to darken it and otherwise affect the surface characteristics; and they will form highly flexible, moistureproof layers or films.

It is therefore an important object of this invention to provide a laminated sheet or web material having as an adhesive layer joining the superimposed laminations a flexible composition that will impart moistureproofness, waterproofness and gasproofness to the laminated article, and that is substantially colorless and odorless.

It is a further object of this invention to provide a laminated sheet material of board, paper, metal foil, fabric and the like, joined by a rubber-paraffin wax adhesive layer of such high viscosity as not to strike through or impregnate the component laminations.

A further object of this invention is to provide a laminated sheet or web material which is light colored, odor-free, printable and glueable and which can be creased or folded without materially impairing its moisture and waterproof characteristics.

Other and further objects of this invention will be evident from the following specification and the accompanying drawing.

On the drawing:

Figure 1 is a diagrammatic side elevational view of a machine for producing our laminated sheet material, with the webs in section and exaggerated as to thickness to show the invention more clearly.

Figure 2 represents a sectional view of our laminated sheet material, with the webs in section and exaggerated in thickness for clarity.

The composition which we use for making our

laminated sheet or web material must have definite characteristics in order to produce a satisfactory product. It should first of all be sufficiently adhesive to unite the layers firmly so that they will not separate during use. The composition should be substantially odorless and tasteless when used for producing food wrappers. Moreover the composition should be colorless, moistureproof, waterproof, and gasproof. In wrapping certain foods such as breakfast cereal foods, it is essential that moisture from the surrounding air should not penetrate through the wrapper and then be absorbed by the contents. Furthermore in certain food packages as in the case of semi-dried fruits or tobacco, it is necessary to retain the moisture within the package in order that the contents do not become too dry. The composition for laminating purposes should therefore prevent the loss of moisture in such cases. Another desirable characteristic of the composition is that it should enable the laminated stock to withstand creasing without substantially impairing its original water-, moisture- and gasproofness.

A further important requirement is that the composition should not penetrate or soak through the laminated sheets or webs to any substantial degree. By preventing such penetration the outer surfaces of the laminated sheets or webs retain their original characteristics so that when using ordinary sulphite stock, for example, they can be readily printed and glued.

We have succeeded in developing a composition which has these and other desired properties. When applied to the paper, web or sheet material, the composition remains primarily as a continuous unbroken surface coating which is thermoplastic, adhesive and flexible.

In preparing our composition we have found that it is possible, by adding suitable binders under controlled conditions to certain thermoplastic substances which are brittle and not flexible at ordinary temperatures, to render such thermoplastic substances pliable and flexible to a remarkable degree. We have, for example, discovered that substances such as paraffin wax which are brittle and not flexible at ordinary temperatures can be rendered pliable and flexible by adding thereto certain binders such as rubber, gutta percha, "Vispronal" (a straight hydrocarbon produced by suitably polymerizing some of the unsaturated hydrocarbon gases produced in cracking petroleum) and similar binding agents.

We have also found that by properly controlling the proportions and compounding conditions, we can uniformly produce compositions having a desired predetermined viscosity and cohesiveness whereby they can be employed as an adhesive for coating or laminating fabrics.

The major ingredient or body of our composition thus consists essentially of a thermoplastic substance which is not flexible or pliable at ordinary temperatures. Such body substance is furthermore solid at normal temperatures, but liquefies at higher temperatures, is insoluble in water and acts as a dispersing medium or solvent for the binder which is added thereto. Any substance having the aforementioned properties can be used for our invention, as, for example, paraffin-wax, beeswax, spermaceti, etc., singly or in combination with one another.

The binder which we add to our body portion is thermoplastic, insoluble in water and solid at ordinary temperatures. It is furthermore elastic, flexible and has strong adhesive properties.

It is dispersible or soluble in the body portion. Any natural or synthetic substances having the aforementioned properties may be used as our binder, as, for example, rubber, balata, gutta percha, "Vispronal" or other artificial gummy or rubber-like substances, singly or in combination with one another.

By properly compounding these substances in suitable proportions and under carefully controlled conditions so as to produce the proper viscosity hereinafter more fully described, we have obtained compositions which have distinctly new properties and are useful for laminating purposes.

When properly compounded so as to have a viscosity of not less than 8000 secs. (time measured on a Scott viscosimeter at 90° C. for a flow of 50 c. c.), the tendency of our composition to strike through paper is minimized with the result that a superficially adherent coating is produced which is flexible, non-tacky, moistureproof, waterproof and gasproof.

A specific embodiment of our composition adapted for laminating purposes comprises a composition of rubber, or a rubber-like substance and a wax, or a wax-like substance. Suitable rubber and rubber-like substances include pale crepe rubber, smoked sheet rubber, vulcanizable rubbers generally and gutta percha. We have successfully used paraffin wax, beeswax, spermaceti, and other waxes, in the preparation of our composition. However, pale crepe rubber and paraffin-wax are the ingredients which we prefer to use, for producing a substantially colorless, odorless and tasteless product.

Since compositions of rubber and wax have widely varying viscosities, depending upon the proportions and particular ingredients used and upon the conditions of preparation, we have found it is of assistance first to determine the limits of viscosity within which the compositions show satisfactory results. In general, a composition to be suitable for laminating purposes should have a viscosity of not less than about 8000 secs. (50 c. c. measured on a Scott viscosimeter at 90° C.). Below this viscosity, there is a tendency of the composition to "strike through" or penetrate the sheet coated therewith.

The ability of a composition to strike through, however, is naturally different with different weights and kinds of paper. The less hydrated and thinner papers require a composition of greater viscosity to prevent penetration, whereas compositions of lower viscosities can be employed with heavier and/or more highly hydrated papers. Consequently, the viscosity of the rubber-wax composition for laminating purposes may be as low as 1000 to 2000 secs. when the composition is to be used with heavier and/or more highly hydrated paper or with other sheet material having greater impenetrability toward the composition.

From a standpoint of good adhesiveness, the viscosity of the rubber-wax composition may be varied through even wider ranges than above indicated, although viscosities above 8000 secs. appear to be preferable. In fact, compositions having viscosities that are too high to be conveniently run on a Scott viscosimeter, for instance above the equivalent of 300,000 secs., exhibit excellent adhesiveness.

In compositions of our invention having up to about 30% by weight of the mixture pale crepe rubber and 70% paraffin wax (at which point the viscosity becomes too great for ready application) the cohesiveness of the mixture and its adhesiveness increase with the viscosity. It is therefore

important not to lower the viscosity of any given mixture unnecessarily, as by increasing the temperature or time of heating of the ingredients when dissolving the rubber in the wax. The viscosity, for a given concentration of rubber in wax, decreases with the time of heating.

As to the effect of temperature on viscosity, we have found that with a given concentration of pale crepe rubber in wax, the viscosity at a given temperature is inversely proportional to the temperature to which the mixture has been heated during or after the solution period. For instance, the effect of temperature on the viscosity of a composition of 6% pale crepe rubber in paraffin-wax was determined by quickly heating the mixture to a given temperature and holding at that temperature for one hour, with the following results:

Temperature (1 hour)	Viscosity (Scott at 90° C., 50 cc.)
150° F.	12000
250	6500
300	1000

With a given concentration of rubber in wax, the viscosity decreases with the time of milling the rubber used in the mixture.

When the percentage of rubber is too low, the composition is not sufficiently flexible and does not have satisfactory adhesive properties for use as a bonding medium in laminating web materials. Also, the viscosity is so low that the composition strikes through the sheet material. When too much rubber is used, the composition is too viscous and is too tough to be a satisfactory adhesive for our purposes.

For this reason we prefer, when using unvulcanized rubber, to keep the percentage of rubber in our composition between 10 and 20%, although some of the advantages of our invention can be obtained with the rubber as low as 6% or as high as 30%, by weight, of the mixture. In the case of gutta percha, the percentage of gutta percha may be increased considerably above 30% without causing too high a viscosity. In general, higher percentages of milled rubber and gutta percha are required to give viscosities corresponding with those obtained by the use of unvulcanized, unmilled rubber.

Pale crepe rubber or smoked sheets may be used most satisfactorily, but pale crepe rubber is preferable because of the odor and color of the smoked sheet. A preferred formula for our composition is as follows:

Paraffin wax	Per cent by weight
(Mpt. 120-180° F.)	85-88
Rubber	
(Pale crepe sheets 0.020 to 0.050 inches thickness)	15-12

The composition must be prepared under carefully regulated conditions which we have determined by long study and experimentation. The paraffin-wax is first melted by heating in a jacketed vessel, preferably provided with a kneader type of stirrer, to a temperature of about 200-210° F. The individual sheets of rubber are then carefully added to the bath so that the surfaces are completely wetted with the molten paraffin as they are being immersed in the bath so as to avoid sticking and welding of the rubber sheets to each other in the bath.

In the case of the lower concentrations of rub-

ber, up to about 15%, there is an adequate volume of wax to facilitate good soaking of the rubber. The main precaution involved in effecting a solution of this kind is a careful addition of the rubber as described and correct mixing procedure. Concentrations of from 10 to 15% rubber have a final viscosity sufficient to pull apart soft lumps of rubber which are not properly soaked; concentrations below 10% rubber in wax do not build up such a high viscosity and consequently rigid precaution must be taken to secure proper soaking.

In considering concentrations ranging from 15 to 25% rubber in paraffin-wax it is necessary to add the rubber quickly so that the rubber added last will have an adequate chance to soak up its share of the wax. This range of concentrations has a resulting high viscosity which enables the batch to pull apart lumps which would ordinarily cause trouble in lower concentrations.

It is necessary to use another method for mixing rubber and paraffin-wax in concentrations above 25% rubber. This method resembles somewhat the present commercial method for compounding rubber. The rubber is "broken down" in the presence of say, an equal weight or less of paraffin-wax. This can be done in several types of mixers like the Banbury or the Werner-Pfleiderer. If a lower concentration is desired paraffin-wax should be slowly added after the original rubber-wax composition has been thoroughly mixed. This method can also be used for procuring low concentrations of rubber in wax by carefully diluting to the desired composition.

During the addition of the rubber in the specific example of our preferred composition the temperature of the bath is permitted to drop to 180 to 190° F. and is maintained at this temperature throughout the compounding operations. After all the rubber has been added, the bath is gently stirred with a paddle so as to permit thorough penetration of the paraffin into the rubber and to prevent lumping of the rubber during solution. This stirring operation is continued for about fifteen minutes until the rubber sheets are adequately soaked.

The mixture is then stirred mechanically in a kneading type of mixer until the batch is free of lumps of undissolved rubber. This operation requires 1½ to 2 hours and the temperature of the mass is maintained at 180 to 190° during the entire period. At the end of this time any undissolved lumps may be strained out, broken up and returned. The composition so prepared is then ready for use.

During the compounding operations it is necessary to keep the temperature of the rubber-paraffin wax mixture at about the temperatures indicated in order to avoid overheating, which results in an undesirable darkening of the mass and imparts an odor to it. However, if some slight color and odor are permissible, temperatures of up to 200 to 220° F. may be employed. Due recognition should be given to the fact that viscosity of the composition drops if the time of heating is prolonged or if higher temperatures are employed.

Various pigments or other coloring matters, fillers, antioxidants and the like, may be incorporated, either directly or by means of a master batch, into the rubber-wax mixture, depending upon the type of pigment, filler or added ingredient to be incorporated. If a white composition is desired, for example, a white pigment such as titanium dioxide, or mixtures of titanium dioxide

with either calcium sulphate or barium sulphate may be incorporated into the composition.

Three general methods of incorporating additional ingredients have been developed by us.

First: Certain pigments, fillers and other materials are mixed directly with the paraffin-wax in quantities up to, say, several percent by weight, such as:

Aluminum powder,
Sulphur,
Sodium salicylate,
Sodium benzoate,
p, p'dioxy diphenyl cyclohexane
(an antioxidant) 10

Second: Other materials which are not "wetted" readily by the wax are incorporated into a master batch with solid wax, say in a 50-50 mixture, using a Banbury mixer or an ink mill. This is true of such pigments as:

Du Pont Red RL (Schultz Index 189)
Du Pont Red TX (Schultz Index 189) 20

Third: Other ingredients to be added are first incorporated in a rubber-paraffin wax master batch which is then added to a previously prepared rubber-wax composition. In this class may be enumerated the following:

Titanium oxide,
Zinc oxide,
Symmetrical di-beta-naphthyl-para-phenylene-diamine,
Hydroquinone 30

The following will serve as an example of our preferred method of incorporating pigment into a rubber-paraffin wax composition, parts by weight being given:

Example

A master batch is first prepared in a Banbury mixer, using pale crepe rubber, paraffin-wax and a titanium dioxide pigment. 40

75 parts of pale crepe rubber are placed in the mixing chamber and the ram is held against the rubber for a sufficient time to break it down, in general, from 3 to 4 minutes, depending on the temperature of the mixture. The ram is removed and 75 parts of the pigment are added while the mixer is running; the ram is then replaced and the pigment and rubber allowed to mix for another period of about 5 minutes. It is essential that adequate mixing be produced before proceeding with the next step. For example, some pigments will mill into the rubber much more readily than others so that the length of milling time must be determined by the experience of the operator. After the pigment is well dispersed in the rubber, 150 parts of solid paraffin-wax are added to the rubber-pigment mixture and the batch is allowed to mix for an additional 5 minutes. During the entire process a stream of cold water is allowed to run through the jacket and the rotors of the mixer to prevent the temperature from rising above, say, 180° F. Before discharging the batch the rubber should be well dispersed in the wax. 65

For incorporation into the ultimate laminating mixture, the master batch of rubber-wax pigment (or other material which it may be desirable to incorporate into the batch) should preferably be rolled into a thin sheet. This may then be added to the mixer in which the rubber and wax are being kneaded together. It is possible to use the master batch without sheeting but considerably longer time is taken to secure proper incorporation into the film forming material. 75

We have found that it is possible to vulcanize our rubber-paraffin wax composition at practically any temperature between say 70° F. and 300° F. However, if such mixtures are vulcanized or even partially vulcanized before use they become highly viscous and gelled so that they cannot be used satisfactorily for coating or laminating purposes. It is also obvious that a high vulcanizing temperature cannot be employed as such temperature would impair the adhesive qualities of the composition. We have overcome this difficulty by the use of super-accelerators which permit vulcanization to take place after the laminating operation is effected. For incorporating the super-accelerator we prefer to use a split batch method, according to which separate batches are prepared, one containing the vulcanizing agent and activator, and the other containing the accelerator, and the two batches mixed just prior to the laminating step. This avoids vulcanization of the rubber content prior to the laminating operation.

Among the accelerators that we have found satisfactory may be mentioned:

- 25 "Butyl Zimate"—a zinc salt of dibutyl dithiocarbamate
- "Zimate"—zinc dimethyl dithiocarbamate
- "R-2"—the reaction product of carbon bisulphide and methylene dipiperidine
- 30 "ZBX"—zinc butyl xanthate
- "552"—piperidine pentamethylenedithiocarbamate.

Antioxidants are also preferably added to the composition whether it is to be vulcanized or not. We have satisfactorily used the following: hydroquinone, para-hydroxy-phenyl morpholine, pyrogallol, and aniline-beta-naphthol.

The following example will serve to illustrate our preferred method of making laminated sheet material in which the bonding agent is vulcanized. Two master batches are prepared, one containing the vulcanizing agent and activator, and the other containing the accelerator. Suitable compositions for the master batches are:

	Percent
Paraffin-wax	50
Rubber	25
Added ingredients—vulcanizing agent or accelerator	25

For convenience the amount of rubber and paraffin-wax introduced with the master batches into the final composition is disregarded.

The master batches are prepared in a Banbury mixer in a similar manner previously described for incorporating pigments in rubber-wax compositions.

For incorporation into the ultimate mixture to be used, the master batches should preferably be rolled into thin sheets. These may then be added to the mixer in which the rubber and wax are being kneaded together. It is possible to use the master batch without sheeting but considerably longer time is taken to secure proper incorporation into the film forming material.

The final batch of rubber-wax composition may suitably have the following proportions by weight of materials:

	Percent
Accelerator	1/2
Sulphur	1/2
Zinc oxide	1/2
Paraffin wax (m.p. 130–2° F.)	83 1/2
75 Pale crepe rubber	15

To prepare such a composition, two batches of paraffin wax-rubber mixture are prepared, each weighing, say, 50 lbs. and each containing one half of the wax and rubber to be present in the final batch, in the proportions as shown in the foregoing formula. Then to one batch is added 1/2 lb. of accelerator, for instance, piperidine pentamethylenedithiocarbamate, in the form of the 25% master batch previously prepared as described; and to the other batch is added 1/2 lb. of sulphur and 1/2 lb. of zinc oxide in the form of the 25% master batch containing these agents.

Each batch is mixed thoroughly. Equal portions of the two batches are then mixed just prior to use on the laminating machine. With the foregoing method, the final mixture will set up or gel to an unworkable condition almost immediately. It is therefore necessary to use the composition as soon as it is made up.

When a milder cure is desired the proportions of accelerator and sulphur used are reduced. For example, in the final batch of the aforementioned example, the accelerator may be reduced to 1/8% and the sulphur to 1/4%. This freshly prepared composition can be kept at not over 180° F. and used any time within eight to ten hours after it is compounded, without gelling sufficiently to render it unworkable.

When transparency is desired it is preferable to use zinc carbonate instead of zinc oxide in the above composition.

Before the final rubber-paraffin wax batch is ready to be put into the hopper of the laminating machine, it may be subjected to a vacuum of 15 to 20 inches of mercury, preferably as high as is practical of attainment, to eliminate air from the batch and to prevent its inclusion in the film formed between the laminations. However this step is not essential as the laminating rolls tend to eliminate any occluded air in the composition.

In preparing our composition for laminating purposes we have found furthermore the following factors are important to control the viscosity and adhesiveness of the product: (1) selection of suitable body substance and binder; (2) proper proportions of these substances; (3) the temperature of compounding; (4) the time of compounding; (5) the physical characteristics of the binder used; (6) the character of agitation of the ingredients; (7) the effect of other added ingredients. These factors must be properly controlled and coordinated in order to produce uniform results.

We have previously disclosed the selection of suitable thermoplastic substances and their proportions. As the proportion of the binder, such as rubber, is increased in our composition, the viscosity of the composition will increase in proportion and the tensile strength of the product is also increased.

As the amount of binder is increased in the mixture the time of heating for producing a predetermined viscosity is increased. For example, the stretch of rubber-wax films between the webs made from mixtures having the same viscosity, but having different amounts of rubber, increases with the rubber content of the mixture.

The temperature of compounding for our preferred rubber-wax composition is 180° to 190° F. but continued heating at this temperature will cause lower viscosity, discoloration and odor. As the temperature is increased, the viscosity is lowered more rapidly in a given time. Heating

of our rubber-wax composition for periods above say ten hours at 180 to 190° is undesirable as it causes discoloration and odor.

In preparing our rubber-wax composition, it is desirable to carry out our operations in the minimum time necessary to effect complete solution of the rubber in the wax to produce a uniform composition. In prolonging the time of compounding the viscosity of the composition is lowered. This also causes a decrease in the tensile strength of the product. Inasmuch as in our preferred composition the mixture is maintained at a temperature of 180 to 190° F., prolonged heating causes discoloration and odor in the mixture.

With given proportions the time of compounding to produce a uniform mixture is determined by the thickness of the rubber sheets used, the temperature of compounding and character of agitation. An increase in the thickness of the rubber sheets used will increase the time of solution. By increasing the temperature, the time of compounding is reduced, but as previously pointed out, too high temperature cannot be employed.

Inasmuch as the rate of solution of the rubber sheets is dependent on the area of rubber subjected to the action of the molten paraffin, the physical formation of the rubber sheets is also an important factor. A thin sheet of pale crepe rubber, for example, contains many spaced small nodules of rubber. In soaking this sheet in a paraffin bath, the paraffin penetrates the spaces between the nodules causing more rapid solution of the rubber than would occur if there were no spaces as in smoked sheet rubber.

We have found that the thickness of the rubber sheets used is important because the thinner the sheets of rubber used, the less time is required to dissolve the rubber. For example, in compounding 15% rubber by weight in paraffin-wax (m. p. 130° F.) at 180° F. using a kneader mixer, the rubber used being bandage pale crepe sheets of 0.015 to 0.020 inches thickness, the time for obtaining complete solution is about one hour. When using a grade of rubber known as RCMA pale crepe rubber sheets having a thickness of 0.030 to 0.040 inches, the time of solution is 1½ to 2 hours under the same conditions. Regular pale crepe having 0.060 to 0.070 inches thickness requires about four hours or more for complete solution under the same conditions. The thickness of the rubber sheets used thus determines the time of compounding which must be carefully controlled and coordinated with the other factors mentioned.

We have found that it is important to regulate the character of agitation in preparing the rubber and paraffin mix. Any suitable means may be used for this purpose such as a kneading type of mixer or ordinary rubber cement mixer. The mixer should be operated so as to effect the complete dispersion of the rubber in the minimum time without substantially breaking down the internal structure of the rubber aggregates in order to avoid reducing the final viscosity below the desired limits. The time of compounding will, of course, be dependent on the type of mixer used.

Continuous mechanical stirring of rubber-wax composition during heating reduces the viscosity as compared to the viscosity of the same composition when stirred only occasionally under the same conditions.

The effect of adding other specific ingredients,

such as accelerators, pigments or fillers, to the body and binder of our composition must be considered in relation to the viscosity and desired characteristics of the final product and properly compensated for by varying the other mentioned factors. The effect of some added ingredients may be to lower the viscosity while other added ingredients may increase the viscosity. For example, additional viscosity may be obtained over that of pure paraffin wax alone by the addition to paraffin of other materials such as aluminum stearate, but the resultant mixture does not have as good adhesiveness nor moistureproofness as a rubber-paraffin mixture of equal viscosity.

The properties of our composition and product are thus entirely dependent upon the proper control of the aforementioned factors which must be carefully coordinated and adjusted for each composition.

Referring now to the drawing, in Fig. 1, the reference numeral 20 indicates a mass of our rubber-paraffin wax composition, for example, which is being drawn between two squeeze rolls 21 and 22 to effect the lamination of the constituent plies 23 and 24. The rolls 21 and 22 should be metal rolls that have been accurately ground to present smooth, equi-spaced surfaces throughout their width. Said plies 23 and 24, which may be any suitable web material, such as paper, are lead over the rolls 21 and 22 from opposite directions and are caused to pass therebetween. The squeeze rolls 21 and 22, which may be suitably heated by steam introduced through pipes 25 and 26, are provided with means (not shown) for adjusting the pressure exerted against the material passing therebetween. After passing between the rolls 21 and 22, the laminated material, indicated by the reference numeral 27 is passed around chill rolls 28 and 29 which are maintained at as low a temperature as is feasible, say 35° F., by means of brine circulating pipes 30 and 31, respectively.

We have found that by chilling the laminated web material as quickly as possible, we obtain a superior bonding film in the laminated product. As contrasted with a slowly cooled film of our wax rubber composition, quick cooling results in a composition of greater flexibility, transparency, stretch, tensile strength and moistureproofness. Hence, in our laminating machine we prefer adequate and very cold chilling rolls set as near as possible to the laminating rolls in order to get the best results.

The bonding composition from the mass 20 is picked up by the surfaces of the web material 23 and 24 as the webs pass into the nip of the rolls. The rolls 21 and 22 are maintained at a sufficiently high temperature to soften the viscous mass of coating material and to permit it to be spread out uniformly over the surfaces of the web. A temperature of from 180 to 220° F is satisfactory. The thickness of the bonding layer is governed by the pressure exerted against the composite web by the rolls 21 and 22.

The laminated sheet material of our invention thus comprises a plurality of constituent plies 23 and 24 of fibrous sheet material and an intermediate bonding layer 30 of our composition. Such laminated sheet material has the advantage of being moistureproof, waterproof and gasproof to a high degree. At the same time, white laminations may be produced by the use of white sheet material for the constituent plies. This is a distinct advantage, since the present

asphalt laminated sheets are dark colored and may have an objectionable odor.

The flexibility of the adhesive seal uniting the laminations is such that the laminated paper or the like can be creased or otherwise distorted without breaking down the moistureproofness and waterproofness of the adhesive layer. Furthermore, the component plies can rarely be separated, when the preferred adhesive composition is used, without rupturing the material of the laminations themselves. In addition a printable and glueable product is obtained.

Where light-weight, translucent or semi-transparent papers are used, such as bleached sulphite, greaseproof, glassine and parchment papers and the like, very satisfactory wrapping paper can be produced having the property of translucency in addition to the other properties aforementioned.

By the practice of our invention we are able to produce many distinct and novel effects not heretofore obtainable. Thus we may produce papers which are highly moistureproof but of white or light color—and which may be printed, glued and otherwise handled like an ordinary sheet of paper. Moreover moistureproofness may be obtained with a relatively small amount of laminating bonding material thereby reducing the weight of the finished product as well as the cost.

We have a further desirable characteristic in that our adhesive is sufficiently thermoplastic so that, where desired on certain types of packaging machines, the sheet may be slightly warmed and thereby made to operate more easily on the machine; yet after application the adhesive will again become harder, thereby stiffening the package.

Moreover we may use waxes of various melting points, thereby obtaining products particularly suitable for certain purposes. Thus if the laminated paper is to be used as tight-wrap on a package (for sterilized prunes where the temperature may be as high as 160° F.) we may employ a paraffin-wax of a high melting point and thereby prevent the gradual penetration of the laminating composition into the paper.

Further we may employ a laminated paper having as bonding material a self-vulcanizing composition of rubber and wax. Thereby we obtain a paper which is more resistant to light and heat and which is therefore preferable for use where it may be subjected to continued exposure to these conditions.

Obviously we may obtain many desirable combinations of fabrics by our laminating compositions, all of which may be light-colored, free of odor, and moistureproof, even when creased or folded. Thus, for example, by laminating a greaseproof paper to an ordinary soda-sulphite paper with our laminating material, we have a product which is greaseproof, moistureproof and flavorproof. Therefore, it is ideal for such products as drink powders, grated cheese and the like since it may readily be formed into suitable bags, envelopes or other containers.

In some cases it may be desirable to have a sheet which is waterproof and moistureproof and yet whose surface is free of adhering wax or similar coating. We may produce this combination by laminating together two—"dry-waxed" papers with our compositions.

We prefer to use sized paper in producing laminated paper sheets. Inasmuch as our bonding layer does not penetrate through the sheets the sizing in the outer surfaces of the sheets serves

to prevent absorption or penetration of any moisture contacting the laminated sheet.

Many other types of combination may be prepared. For example, we may laminate transparent cellulose sheeting to a sulphite or like paper, thereby producing a sheet of high finish and gasproofness; and of exceptional moisture resistance when moistureproof sheeting is employed. We may produce a vari-colored adhesive by combining batches of different colors just previous to laminating, thereby producing novel ornamental effects in the finished sheet.

We may add white pigments such as titanium dioxide to our laminating material, since there is no tendency for them to settle out, due to the high viscosity of our mixture. A laminated sheet prepared with such a mixture will have unusual whiteness and opacity, particularly if opaque papers be used in this combination.

We may laminate papers to boards with our composition thereby imparting the desired moistureproofness which is retained even on scoring and bending, as in a carton. We may also laminate metal foils to paper with our composition.

Numerous other laminated combinations may be mentioned, all of which may have the desired characteristics of light color, strong adhesion, freedom from odor and excellent moistureproofness even when creased or folded.

The term "rubber" as used in the appended claims is intended to include the use of india rubber (such as pale crepe rubber and smoke sheet rubber), gutta rubber, synthetic rubber or other artificially produced gummy substances which are suitable for the purpose of this invention, singly or mixtures thereof.

The term "wax" as used in the appended claims is intended to include the use of paraffin-wax, beeswax, spermaceti, candelilla, carnauba and their natural or synthetic equivalents, or mixtures thereof, suitable for the purpose of this invention.

Although we have described our invention in detail and, therefore, utilized certain specific terms and language herein, it is to be understood that the present disclosure is illustrative, rather than restrictive, and that changes and modifications may be resorted to without departing from the spirit or the scope of the claims appended hereto.

We claim as our invention:

1. Laminated sheet material which is waterproof, moistureproof, gasproof, light color, odorless, glueable and printable, the layers of same being united by a continuous flexible film formed from a composition comprising wax, rubber, a vulcanizing agent, accelerator and activating agent, having an initial viscosity of at least 8000 secs. (Scott viscosimeter at 90° C.)

2. Laminated sheet material which is waterproof, moistureproof, gasproof, light color, odorless, glueable and printable, the layers of same being united by a continuous flexible film formed from a composition comprising wax, rubber, a vulcanizing agent, accelerator, activator, pigment, and an age resistor, having an initial viscosity of at least 8000 secs. (Scott viscosimeter at 90° C.,

3. Laminated sheet material which is waterproof, moistureproof, gasproof, light in color, odorless, glueable and printable, the layers of same being united by a continuous flexible film formed from a composition comprising wax, rubber and a pigment.

4. Laminated sheet material comprising con-

- stituent plies of sheet material having a bonding layer therebetween of a thermoplastic composition comprising from 6 to 30% of pale crepe rubber and from 94 to 70% of paraffin-wax, the viscosity of said composition being sufficiently high so that the composition does not strike through the constituent plies.
5. Laminated sheet material having an intermediate moistureproof, waterproof and gasproof bonding layer comprising a solution of 6 to 30% of rubber and 94 to 70% of wax, said composition having a viscosity of over 8000 secs. (Scott).
6. A translucent, flexible laminated wrapping paper comprising plies of greaseproof paper having a bonding layer therebetween of a rubber-wax composition.
7. A wrapping paper comprising laminations of paper permeable by wax alone and a bonding layer joining said laminations comprising a mixture of from 6 to 30% rubber and from 94 to 70% wax, said mixture having a sufficiently high viscosity that it will not penetrate said paper laminations.
8. Laminated sheet material having a vulcanized rubber-wax composition bonding layer between the constituent plies.
9. Laminated sheet material having a vulcanized rubber-wax composition bonding layer between the constituent plies, said composition comprising from 6 to 30% of rubber and from 94 to 70% of wax.
10. Laminated sheet material comprising constituent plies of paper having a vulcanized rubber-wax composition bonding layer between the constituent plies.
11. Laminated sheet material comprising constituent plies of paper having a vulcanized rubber-wax composition bonding layer between the constituent plies, said composition comprising from 6 to 30% of rubber and from 94 to 70% wax.
12. Flexible, moisture-, water- and gasproof laminated sheet material suitable for wrapping purposes comprising constituent plies of wrapping paper having a bonding layer therebetween of a vulcanized rubber-wax composition containing an antioxidant.
13. Flexible, moisture-, water- and gasproof laminated sheet material suitable for wrapping purposes comprising constituent plies of wrapping paper having a bonding layer therebetween of a vulcanized rubber-wax composition containing a pigment.
14. Flexible, moisture-, water- and gasproof laminated sheet material suitable for wrapping purposes comprising constituent plies of wrapping paper having a bonding layer therebetween of a rubber-wax composition containing an antioxidant.
15. Laminated sheet material which is water-proof, moistureproof, and gasproof, the layers of same being united by a continuous, flexible film formed from a composition comprising a body portion and a binder portion intimately mixed therewith, said body portion comprising wax and said binder portion comprising rubber.
16. Laminated sheet material which is water-proof, moistureproof, and gasproof, the layers of same being united by a continuous flexible film formed from a composition comprising a body portion and a binder portion intimately mixed therewith, said body portion comprising wax and said binder portion comprising "Vis-pronal".
17. Laminated sheet material comprising a ply of sheet material and a sheet of metal foil united thereto by a bonding layer of a rubber-wax composition.
18. Laminated sheet material having a bonding layer therebetween comprising wax, rubber and an antioxidant.
- ALLEN ABRAMS.
CHARLEY L. WAGNER.
GEORGE W. FORCEY.

DISCLAIMER

2,054,116.—*Allen Abrams, Charley L. Wagner, and George W. Forcey, Wausau, Wis.*
LAMINATED SHEET MATERIAL. Patent dated September 15, 1936. Disclaimer filed May 20, 1938, by the assignee, *Marathon Paper Mills Company*.
Hereby disclaims from the scope of claim 16 of said patent any composition except such in which the body portion constitutes a major ingredient of the composition.
[Official Gazette June 14, 1938.]

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