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PREPARATION OF SHEET MATERIAL WITH
REMOISTENABLE GUM COATINGAustin E. Davis, Nashua, N. H., assignor to
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chusettsNo Drawing. Application May 25, 1950,
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5 Claims. (Cl. 117-122)

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This invention relates to the production of such articles as labels, of which the common postage stamp is the most familiar example, gummed tape and like products consisting of a base sheet having a thin film-like coating of dried adhesive, "gum," thereon, which film when moistened by water becomes adhesive so that the article can be stuck to something else.

The object of the invention is to provide a method for the preparation of such an article having a uniformly distributed thin film of gum which, although appearing to the naked eye (megascopically) as a continuous, homogeneous layer extending throughout the area of the coated article, is in fact minutely porous or cellular. An article having a gum coating of this character is advantageous for various reasons. It may be more readily activated by moistening, since the water will enter more quickly to an adequate depth. There is a certain unavoidable delay between the moistening of such a gum layer and its application in proper position. During this interval the moistened gum begins to dry, sometimes becoming too firm to be properly adhered. With the porous layer, satisfactory gumming may be attained after significantly longer periods of delay. Since such an adhesive is of lesser density than the conventional coating of the prior art, its apparent volume is greater, so that a lesser amount, by weight, is as effective as a greater amount employed as a solid layer. This may be explained as follows. The foundation papers commonly employed have significant surface irregularities and are relatively porous so that in normal gumming a considerable amount of glue serves only a surface-filling function. To obtain good adhesive contact with another surface there must be a certain excess beyond this surface-filling portion. The amount required, by weight, of porous glue for surface-filling is less and also the excess required, if of porous glue, is less. Furthermore, since moistening is more deeply effected in porous glue, even with a lesser amount of dry adhesive there is a greater amount of usefully moistened adhesive.

The adhesives most commonly employed for the production of articles of the kind under consideration have been animal glue and starch products such as dextrans. Gum arabic, polyvinyl alcohols, and other materials which become usefully tacky when wet with water have also been employed. In this application such water activatable materials are for simplicity referred to as "gum." This corresponds to the popular usage.

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The gum coating on labels, gummed tape and similar articles is thin. The amount of gum is commonly expressed in terms of weight per ream of 3,000 square feet. In the case of ordinary gummed tape a coating of about fifteen to twenty-five pounds per ream is common and this corresponds to a thickness of about one or two mils. A postage stamp has a thinner layer of gum. A minutely cellular or porous coating of lesser density will weigh less for a given thickness or have a greater thickness for a given weight. In any instance the thickness is small and ordinarily would not exceed a few mils. Herein the word "thin" as applied to the adhesive coating is intended to exclude coatings more than fifty pounds per ream.

It is believed that an understanding of the invention will be facilitated by a brief sketch at this point, which should not be understood either as a complete exposition thereof or as a definition of scope, the former being provided by the specification as a whole and the latter by the annexed claims, when read and understood in the light of the specification. Briefly, my invention contemplates a gradual liberation of gas in the fluid coating composition after it has been applied to the paper, this liberation being effected either by single or double decomposition of materials incorporated in the coating composition, with the liberation of the gas occurring gradually as the coating sets, so that there is retained in the dried film substantially throughout its volume multitudinous voids, largely of microscopic dimension. These results are obtained in a thin film of the kind under consideration without collapse of the gas-expanded film because of premature formation and consequent release of gas bubbles while the film is still fluid and also without disruption of the film due to too vigorous gas formation.

I am aware that the production of material in the form of a porous or spongy mass by the internal evolution of gas, notably carbon dioxide, is broadly speaking, well known. It is frequently effected when the material is confined in a mold which prevents the escape of the gas, or a mass of large dimension and of initially doughy consistency from which the gas escapes only with difficulty is treated. In contrast, we are here concerned with a thin layer as above defined, having a free surface of large area and initially, to permit it to be coated on the paper, the composition is fluid. Obviously the evolution of gas cannot occur before the adhesive composition is applied to the backing material. Also, it must not occur rapidly so that the gas escapes from the adhe-

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sive film while it is still highly fluid. Also, it must not disrupt the film after it has become more or less viscous. The resultant porosity must be of a minute character, substantially microscopic, as otherwise the resultant film would be too fragile and too readily rubbed off before and during subsequent moistening of the gummed material. The processes which I am about to describe satisfy these requirements.

For use as the gas by which porosity is attained, carbon dioxide is the most obviously useful, since it is economical, insoluble, nonflammable and innocuous, and I shall therefore confine my examples thereto.

I shall first give an example wherein the gas is evolved by double decomposition. Otherwise stated, the gas is liberated by a metathetical or ion-interchange reaction.

EXAMPLE 1

(A)

85 parts by weight bone glue (220 gram jelly strength)

85 parts by weight water

Heat the above to a temperature preferably of about 52 degrees centigrade or higher to effect complete solution of the glue. Cool, if necessary, to not over 52 degrees centigrade and adjust to a pH of 8.5 by addition of ammonia.

Make, separately, a solution of the following:

(B)

7½ parts by weight citric acid

10 parts by weight 26° Baumé ammonia.

Let dissolve until reaction is complete. Test for pH and bring to a pH of 9.0 if necessary by the addition of 26° ammonia.

Add to solution B the following:

(C)

7½ parts by weight sodium bicarbonate

65 parts by weight water.

Adjust the combined solutions of (B) and (C) to a temperature of approximately 52 degrees centigrade and add to solution (A).

In the coating composition prepared as above described there is a salt, sodium bicarbonate, which may be decomposed to liberate carbon dioxide and an acid, citric acid, effective for that purpose. However the reaction will not occur so long as a pH of 8.5 or higher is maintained by the presence of an excess of ammonia. The ammonia is an inhibitor of the reaction.

The composition may be coated on paper in accordance with the usual practices of the art and led through a dryer of ordinary form. The gum during drying gradually becomes more and more viscous and is completely set or dry at the completion of the operation. During the drying also the fugitive ammonia is driven off and as soon as some is dissipated the pH value is lowered. Some of the acid then reacts with the carbonate, releasing carbon dioxide gas. As the result of this acidity is reduced and the reaction tends to stop, but as more ammonia is dissipated it resumes. The rate of heating is important. I have found that if the pH of the composition before coating is maintained between 8.5 and 9.0, the rate of evolution of carbon dioxide can be suitably controlled for the purposes of the invention by maintaining a drying temperature within the range of 75 to 95° C.

As it gradually becomes more rigid the gum

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layer is leavened and sets in the desired minutely porous or cellular form. Some of the bubbles of gas may break through to the surface, but in general there is no disruption of the film on a large scale. Other bubbles may be trapped and either remain as such or escape by diffusion, being replaced by air. Collapse of the expanded film on the one hand, or its essential disruption on the other is avoided. The inflated mass of viscous gum may be considerably altered in structural form during the process before its final set, but in general it preserves the character of a continuous phase exhibiting substantially microscopic voids dispersed throughout its volume.

I shall now give an example different from Example 1 in that there is utilized instead of a dissolved soluble carbonate, a water insoluble carbonate dispersed throughout the otherwise liquid coating composition in the form of finely divided solid particles.

EXAMPLE 2

(A)

1 part by weight bone glue (220 gram jelly strength)

10 parts by weight water

Heat the above to a temperature preferably of about 52 degrees centigrade or higher to effect complete solution of the glue. Cool, if necessary, to not over 52 degrees centigrade and adjust to a pH of 7.0 by addition of ammonia.

Add to solution (A) the following:

(B)

5 parts by weight calcium carbonate

The calcium carbonate is dispersed in the glue solution (A) by any suitable means, conveniently by grinding in a ball mill. Effective dispersion can be effected by grinding for about eight hours. Longer grinding does not appear significantly to affect the results. The glue in solution (A) serves as a dispersion agent, facilitating the suspension of the finely divided carbonate particles in the water phase.

The dispersion is then heated to approximately 52 degrees centigrade.

Make, separately, the following:

(C)

84 parts by weight bone glue (220 gram jelly strength)

84 parts by weight water

Heat the above to a temperature preferably of about 52 degrees centigrade or higher to effect complete solution of the glue. Cool, if necessary, to not over 52 degrees centigrade and adjust to a pH of 7.0 by addition of ammonia.

Add to (C) the ground, heated composition of (A) and (B).

Prepare, separately, the following:

(D)

10 parts by weight citric acid

9 parts by weight ammonia (26° Baumé)

Let the above dissolve until the reaction is complete. Test for pH and bring to a pH of 7.0, if necessary, by the addition of 26 degrees ammonia.

Add (D) to the above composition of (A), (B) and (C).

Evolution of carbon dioxide gas will not occur as long as a pH of 7.0 or higher is maintained.

The composition prepared as described is coated on paper and heated. The ammonia is gradually driven off, permitting the gradual evolution of carbon dioxide, as in the previous case. If the pH of the composition before coating is maintained at approximately 7.0, the rate of gas evolution can be suitably controlled for the purposes of the invention by maintaining a drying temperature of approximately 105 degrees centigrade. This temperature is higher than in the case of Example 1, probably because the reaction rate is slower when the acid is attacking a solid, as contrasted with an ionized salt present in solution.

Since sodium carbonate is readily available and is cheap its use in the form of a solution is considered more satisfactory than the use of suspended calcium carbonate and is to be recommended.

Similarly, ammonia is most serviceable as an inhibiting ingredient. Ethylene diamine and hydroxylamine may be instanced as ingredients chemically equivalent for the purpose.

My third example illustrates gas generation by simple decomposition of a chemical compound by heat.

EXAMPLE 3

(A)

100 parts by weight bone glue (220 gram jelly strength)

100 parts by weight water

Heat the above as in Example 1 to dissolve and adjust similarly the pH.

Prepare separately the following solution:

(B)

4 parts by weight ammonium bicarbonate
25 parts by weight water

Adjust the pH with ammonia to 9.0. Bring the temperature approximately to 52 degrees C. and add to solution (A).

This composition will remain stable at ordinary temperatures as long as a pH of 9.0 is maintained.

When this composition is coated on paper and dried a certain amount of the ammonia is first evaporated, permitting the decomposition of the ammonium bicarbonate to commence with resultant evolution of carbon dioxide, which reaction tends to re-establish the stability of the system which is again unbalanced as more ammonia is evaporated. At a drying temperature between 80 and 100 degrees centigrade the decomposition may be made to take place gradually, and its rate readily controlled.

The process of Example 3 as contrasted with those of Examples 1 and 2 leaves no residual material in the dry gum film. The adhesive quality of such a product is somewhat superior to that of the product of Examples 1 and 2, wherein sodium citrate and calcium citrate respectively remain as reaction by-products.

The nature of the product as contrasted with one having the conventional solid gum coating as utilized in the prior art is indicated by the following tests. The material referred to in these tests was prepared as in Example 3.

(a) Tackiness of adhesive

This test (ASTM Method D773-44-T) expresses the tackiness of the adhesive immediately after

the tape has been wet and applied to a standard paper.

Designation	Adhesive per Ream, Pounds	Adhesive Value (2" width)
Solid coating.....	26	46.9 (44 to 52)
Coating under Example 3.....	14	46.9 (44 to 50)
Do.....	16	58.1 (55 to 62)
Do.....	21	62.5 (59 to 65)
Do.....	25	76.3 (72 to 79)

(b) Quality of adherence

This test is a measure of the effect on eventual adherence when freshly moistened tape is allowed partially to dry for varying intervals before it is applied to standard paper. The longer it remains effectively moist the more broadly useful in this respect a given tape will be.

Tapes prepared as in Example 3 and having from 14 to 25 pounds of adhesive, respectively, were compared with tape having a solid coating of 26 pounds of adhesive applied at intervals of 12, 24 and 36 seconds after moistening. The applied tapes were let thoroughly dry and then removed, judging the degree of adherence by the area of standard paper that was torn on removal. The tapes exemplifying the invention at 24 seconds were generally superior to the solid coated tapes at 12 seconds and at 36 seconds were generally superior to the solid coated at 24 seconds.

The proportions of ingredients and the temperatures specifically referred to in the examples given are not sharply critical, but are practical and preferred examples which I give in order to disclose the best mode in which I have contemplated applying the invention. Variations may be worked out under routine laboratory checking procedures.

In the examples mentioned I have referred to animal bone glue of 220 gram jelly strength as the adhesive ingredient. I have found that glues of lower and higher jelly strength may be usefully employed. Hide glues and other adhesive materials commonly used as remoistening adhesives may be substituted, subject to slight variations in the conditions of operating the process, again subject to determination by routine laboratory checking not requiring the exercise of invention.

I am aware that the invention may be embodied in other specific forms without departing from the spirit or essential attributes thereof, and I therefore desire the present embodiment to be considered in all respects as illustrative and not restrictive, as is in fact clear in several matters from the description itself. Reference is to be had to the appended claims to indicate those principles of the invention exemplified by the particular embodiment described and which I desire to secure by Letters Patent.

I claim:

1. The method of preparing sheet material having adherent thereto a thin, minutely porous film of solidified gum adapted on water moistening of the surface of the film to develop an adhesive tackiness therein comprising preparing a coatable aqueous solution of the gum, adding thereto material in itself decomposable under the conditions of drying with resultant evolution of carbon dioxide gas together with a volatile ingredient of high pH value inhibitive of such decomposition and volatilizing under the conditions of drying, coating the sheet material with

a thin film of the so prepared composition and drying the film to dissipate the inhibiting ingredient gradually with consequent gradual evolution of gas concurrently with the setting of the gum.

2. The method of preparing sheet material having adherent thereto a thin, minutely porous film of solidified gum adapted on water moistening of the surface of the film to develop an adhesive tackiness therein comprising preparing a coatable aqueous solution of the gum, adding thereto a salt and an acid capable of reaction to liberate gas together with a volatile ingredient of high pH value to inhibit the reaction, coating the sheet material with a thin film of the so prepared composition and drying the film to dissipate the volatile ingredient gradually with consequent gradual reaction of the salt and acid to evolve gas concurrently with the setting of the gum.

3. The method of preparing sheet material having adherent thereto a thin, minutely porous film of solidified gum adapted on water moistening of the surface of the film to develop an adhesive tackiness therein comprising preparing a coatable aqueous solution of the gum, adding thereto a salt which on heating in solution form will undergo single decomposition with a resultant liberation of carbon dioxide gas together with a volatile ingredient of high pH value inhibitive of such decomposition, coating the sheet material with a thin film of the combined solution and drying the film to dissipate the volatile ingredient gradually with constant gradual decomposition of the salt to evolve gas concurrently with the setting of the gum.

4. The method of preparing sheet material having adherent thereto a thin, minutely porous film of solidified gum adapted on water moistening of the surface of the film to develop an

adhesive tackiness therein comprising preparing a coatable aqueous solution of the gum, adding thereto a carbonate and an acid together with ammonia to maintain a pH value of about 8.5 or higher, coating the sheet material with a thin film of the so prepared composition and drying the film to dissipate the ammonia gradually with consequent gradual decomposition of the carbonate concurrently with the setting of the gum.

5. The method of preparing sheet material having adherent thereto a thin, minutely porous film of solidified gum adapted on water moistening of the surface of the film to develop an adhesive tackiness therein comprising preparing a coatable aqueous solution of the gum, adding thereto ammonium carbonate together with an excess of ammonia to maintain stability of the carbonate, coating the sheet material with a thin film of the so prepared composition and drying the film to dissipate the ammonia gradually with consequent gradual decomposition of the carbonate concurrently with the setting of the gum.

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