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PREGUMMED HANGING MATERIAL

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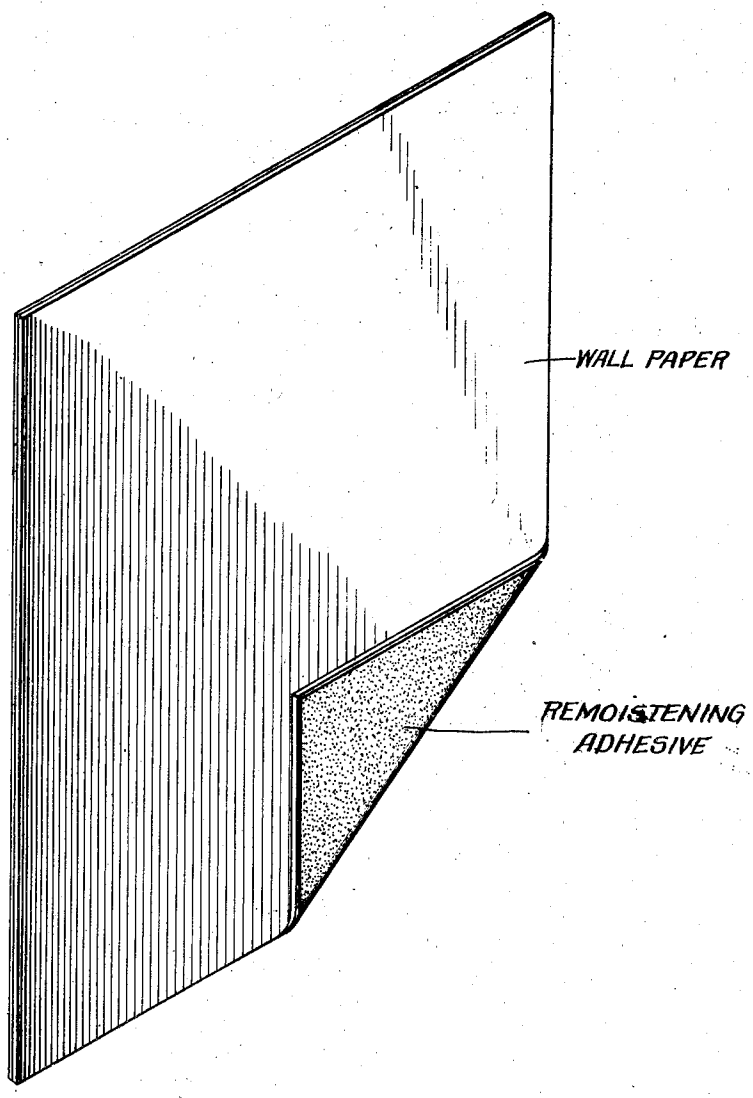

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PREGUMMED HANGING MATERIAL

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1

This invention relates to pregummed hanging materials, more particularly wallpapers, poster papers, billboard papers, canvas wall coverings, thin wooden panels, or other types of hanging materials having a dried coating of adhesive thereon which requires only moistening to be applied to a wall or other surface.

Lobdell Reissue Patent No. 10,430 described a wallpaper which is dry sized on its back and, according to the patent, may be hanged by moistening the sized surface and applying it to a wall. The sizing used is said to be dextrine, glue, paste, or gums. No practical or suitable pregummed hanging paper ever resulted from the teaching of the Lobdell patent because the problem of making a pregummed hanging paper is not so simple that it may be done merely by adding an ordinary type of sizing material or glue to the back of the paper and drying it. A pregummed hanging material, such as a pregummed wallpaper, must have certain characteristics which cannot be obtained with an ordinary adhesive. Excellent pregummed hanging papers and other pregummed hanging materials have been made in accordance with the teaching of U. S. Patents 2,183,532 and 2,215,848 granted to Hans F. Bauer.

One of the objects of the present invention is to provide a new and improved pregummed hanging material in which the remoistening adhesive thereon is made from readily available raw materials.

Another object of the invention is to provide a new and improved pregummed hanging material in which the remoistening adhesive is derived from a cereal flour treated in a particular way, as more fully hereinafter described.

A further object of the invention is the preparation of new and improved adhesive materials.

Other features and advantages of the invention will be apparent by reference to the following specification and the accompanying drawing, in which the single figure represents a pregummed hanging material comprising a wallpaper having a self-contained or dried adhesive coating on the back thereof, as herein described.

In accordance with the invention, we have found that by converting cereal flours, e. g., wheat or rye flours, with small amounts of starch hydrolizing enzymes under specified conditions, an adhesive product is produced which is a very effective remoistening adhesive for use in wallpaper or other hanging materials. We have found that the protein component of wheat or rye flour is of particular value in contributing to the peculiar characteristics required for an adhesive for

2

this purpose. In order to be suitable for this purpose, it is necessary that the adhesive product will meet the following requirements:

1. It must be of such a nature that it can readily be applied to the wall paper stock by a coating mechanism and then subsequently dried without making the sheet brittle or causing it to curl unduly.

2. The adhesive coating should remoisten readily when water is applied to the coated sheet but should not be of such a soluble nature as to wash off of the paper under normal conditions of handling.

3. The remoistened adhesive film should be of a slippery, slow drying character so that when the moistened wallpaper is applied to the wall, it can be readily slid into the proper position to butt the edges and match the pattern.

4. The remoistened adhesive film must be sufficiently slow drying that it will not set up to a non-slippery condition in the time interval that normally elapses between remoistening the sheet and applying it to the wall.

5. After the sheet has been applied to the wall, the adhesive must dry out without causing the sheet to pucker or wrinkle and give a firm bond on any surfaces to which hanging papers are normally applied.

To meet the above requirements we find that it is desirable to convert the flour to such an extent that the viscosity of the final product lies within the range specified herein. It is also desirable in order to obtain the necessary slow drying characteristics that the amylaceous content of the flour be hydrolized to such an extent that a substantial amount of reducing sugars are formed. The slow drying and non-curling characteristics of the adhesive may be further improved by the addition of various soluble salts or other materials which act as plasticizers.

Examples of such soluble salts and plasticizing material which can be effectively used both to slow down the rate of drying and also reduce the tendency of the coated sheet to curl are sodium chloride, sodium formate, sodium nitrate, sodium lactate, urea, glycerine, glucose, invert sugar, etc.

Under the conditions of preparation herein outlined, the protein component of the flour contributes greatly to the slippery characteristic desired in the adhesive. Furthermore, it appears to act as a desirable supplement to the reducing sugars formed during the conversion and the added plasticizing materials in reducing the curling tendencies of the dried coated sheet.

We have found that the percentage of reducing sugars formed as a result of the hydrolization of the amylaceous content of the flour and the viscosity of the final converted adhesive product are the determining factors as to its suitability for our purpose.

For the purposes of our invention, it is desirable that the degree of conversion be such that the final adhesive product shows a reducing sugar content of at least 5% on a dry basis calculated as dextrose, and a viscosity when diluted with water to bring the ratio of solids to water to 1 part of solids to 10 parts water, between 15 centipoises and 750 centipoises at 75° F.

The method used to determine reducing sugars is the approximate volumetric method disclosed in Methods of Analysis of the Association of Official Agricultural Chemists, third edition (1930), chapter XXXIV, sections 31, 32, 33, page 377.

For the purpose of determining viscosities, the Brookfield viscosity apparatus was used.

It is desirable that the adhesive as applied to the paper or other base material, contain not less than 1 part of water nor more than 5 parts of water per 1 part of solids. The ratio of solids to water should preferably not be less than about 1 to 1 for an adhesive of this type if the proper degree of adhesiveness and slip characteristics is to be attained when the adhesive film is remoistened. On the other hand, if the ratio of water to solids is greater than 5 to 1, the amount of drying required in order to apply the adhesive properly to the paper or other material which is to be coated will normally be prohibitive.

From the standpoint of convenience in applying the adhesive to the paper or other material, it is desirable that the adhesive have sufficient fluidity that it may be picked up and applied in a uniform film to the paper by means of the applicator rolls of the coating machine. At the same time, however, the adhesive must have sufficient viscosity that it will not soak into the paper and leave little or no effective adhesive film on the surface of the sheet. With this consideration in mind, it has been found desirable that the viscosity of the adhesive as applied to the paper be adjusted to somewhere within the range of 400 to 13,000 centipoises at 100° F. as determined by the Brookfield viscosity apparatus.

For the more common types of coating devices, a viscosity of between 1200 and 2000 centipoises at 100° F. was found to be very suitable.

The use of acids as well as enzymes of the alpha amylase type or mixtures of enzymes of the alpha and beta amylase types to convert starch to dextrines and sugars is well known to the art. To our knowledge, however, the adhesive herein disclosed represents a hydrolized flour and plasticizer combination having unique remoistening and slip properties that have not previously been anticipated.

For the purposes of our invention, the converting enzymes used may be one or more of the commercially produced enzymes of the alpha or alpha and beta amylase types added to the flour composition in the proper proportions to attain the specified degree of conversion, or if desired, advantage may be taken of the enzymes of this type which are naturally present in wheat or rye flours, particularly those milled from sprout damaged grain, and blending them with such proportions of flour milled from sound grain that a final flour mixture having the proper amount of enzyme present will be obtained.

This latter procedure has the advantage of lower cost and furthermore offers a means of utilizing a substantial proportion of flours that are not suitable for most food purposes.

As an alternative, acids may be used instead of enzymes as a means of hydrolizing the flour to the degree herein specified. The use of enzymes, however, is preferable because of the greater convenience in handling.

It will be apparent to those familiar with the art that the enzyme strength needed to obtain a particular degree of conversion cannot be generally defined because of the many factors which affect the activity of the enzymes. The examples herein, however, illustrate what we have found to be satisfactory practice under the conditions involved.

For the purpose of more completely illustrating our invention, we specify in the examples below the degree of enzyme strength used to obtain the results disclosed. In view of the above, however, we wish to point out that our invention is not limited by the amounts of enzymes or type of converting agent used in these particular examples, but rather by the reducing sugar content, the viscosity limits and the proportion of solids to water herein generally specified.

Example I

This example illustrates the manner in which a remoistening adhesive suitable for the manufacture of prepasted wallpaper was prepared from a white rye flour milled from sprout damaged grain.

The rye flour used in this particular example had an enzyme activity of 2.41 units of alpha amylase as determined by the Kneen & Sandstedt method (Cereal Laboratory Methods, 4th ed., page 96 (1941)). Seventy-seven and seven-tenth (77.7) pounds of the above-mentioned rye flour was dispersed in 100 pounds of water and heated in a steam jacketed mixing kettle to a temperature of 160° F. The mixture was then held at this temperature for twenty minutes, during which time the enzyme present converted the mixture to a fluid consistency. At the end of this period the temperature was raised to 190° F. and held at this point for ten minutes. Then 16.5 pounds of urea, 3.4 pounds of sodium acetate, and 2.4 pounds of zinc sulphate were added to the mixture, and it was allowed to cool for use. The resultant adhesive product tested 26% reducing sugars calculated as dextrose on a dry basis and had a Brookfield viscosity of 1800 centipoises at 100° F. When applied to wallpaper stock on the basis of a dry coating weight of 14 to 16 pounds per ream, it gave an effective prepasted hanging paper which when remoistened, had the slow drying and slip characteristics which are necessary for this purpose.

The adhesive disclosed in this example, when diluted with water to bring the ratio of solids to water to 1 to 10, had a Brookfield viscosity of 16 centipoises at 75° F.

Example II

This example illustrates the manner in which an adhesive suitable for prepasted wallpaper was prepared from a rye flour having an alpha amylase activity of .29 unit as determined by the method of Kneen & Sandstedt, supra. Seventy-eight and four-tenth (78.4) pounds of the above-mentioned rye flour, 16.1 pounds of urea, and 3.3 pounds of sodium acetate were dispersed in 500 pounds of water and heated in a steam jacketed kettle to a temperature of 160° F. The mixture was held at this temperature for twenty minutes.

At the end of this period, the temperature was raised to 190° F. and held at this point for ten minutes. Then 2.2 pounds of zinc sulphate was added and the mixture allowed to cool for use. The resultant adhesive product tested 5.4% reducing sugars calculated as dextrose on a dry basis and had a Brookfield viscosity of 1600 centipoises at 100° F. When applied to wallpaper stock on the basis of a dry coating weight of fourteen or sixteen pounds per ream, it gave an effective prepasted hanging paper which when remoistened had the necessary slow drying and slip characteristics.

The adhesive disclosed in this example when diluted with water to bring the ratio of solids to water to 1 to 10, had a Brookfield viscosity of 715 centipoises at 75° F.

Example III

This example illustrates the manner in which a wallpaper adhesive was prepared from a blend of white rye flours having an alpha amylase activity of .43 unit as determined by the method of Kneen & Sandstedt, supra.

	Pounds
Rye flour blend (alpha amylase .43)	82
Urea	15
Sodium acetate	3

were dispersed in 225 pounds of water. The mixture was heated with direct steam at such a rate that the temperature was brought from 80° F. to 190° F. in a period of 40 minutes. During this heating period the enzyme present converted the mixture to a fluid consistency. After the temperature reached 190° F., 4 ounces of soda ash and 6 ounces of phenol were added to the mixture, and it was allowed to cool down to room temperature.

The resultant adhesive tested 14.0% reducing sugars calculated as dextrose on a dry basis and had a Brookfield viscosity of 1300 centipoises at 100° F. When diluted with water to bring the ratio of solids to water to 1 to 10, the viscosity as determined by the Brookfield viscosity apparatus was 25 centipoises at a temperature of 75° F. The adhesive was satisfactory for prepasted wallpaper and had the necessary slow drying and slip characteristics for this purpose.

Example IV

This example illustrates the manner in which a wallpaper adhesive is prepared from a white rye flour wherein the flour is previously treated with paraformaldehyde to improve its dispersibility in water.

The pretreatment of the flour consisted of blending the rye flour with $\frac{1}{10}$ of 1% paraformaldehyde, and then heating it at a temperature of 220° F. for about 1½ hours.

To prepare the adhesive using this pretreated flour, the following procedure was used:

	Pounds
The above pretreated rye flour	81.4
Urea	15.0
Sodium acetate	3.0
Amyliq N (a commercial enzyme manufactured by Wallerstein Company, Inc., New York	.6

The above materials were dispersed in 250 lbs. of water and the mixture heated to 167° F. It was held at this temperature for 20 minutes and then raised to 200° F. for ten minutes. At the end of this time the mixture was diluted with an additional 100 pounds of water and 4 ounces of soda ash and 8 ounces of phenol were added. The adhesive was then ready for use.

The finished adhesive as prepared above tested 12.3% reducing sugars calculated as dextrose on a dry basis and had a Brookfield viscosity of 1620 centipoises at 100° F. When diluted with water to bring the solids to water ratio to 1 to 10, it had a Brookfield viscosity of 40 centipoises at 75° F.

The adhesive thus prepared was slow drying on being remoistened and had excellent slip characteristics. Good results were obtained when dried coatings of the adhesive were formed on wallpaper in the preparation of pregummed hanging papers.

Example V

This example illustrates the manner in which a wallpaper adhesive was prepared from a white rye flour having an alpha amylase activity of .40 unit and a malted wheat flour having an alpha amylase activity of 17.0 units as determined by the Kneen and Sandstedt method, supra.

	Pounds
White rye flour (alpha amylase .40)	84.7
Malted wheat flour (alpha amylase 17.0)	5.0
Salt (NaCl)	10.0
Powdered whiting (calcium carbonate)	.3

were dispersed in 200 lbs. water. The mixture was heated with direct steam at such a rate that the temperature was brought from 80° F. to 190° F. in a period of 40 minutes. After the temperature reached 190° F., 4 ounces of soda ash and 6 ounces of phenol were added to the mixture and it was allowed to cool down to room temperature. The resultant adhesive tested 16.0% reducing sugars calculated as dextrose on a dry basis. The viscosity of the adhesive as determined by the Brookfield viscometer was 1400 centipoises at 100° F. When diluted with water to bring the solids to water ratio to 1 to 10, it had a Brookfield viscosity of 21 centipoises at 75° F.

Excellent remoistening adhesive coatings on wallpaper and other hanging materials were obtained by applying a layer or coating of the wet adhesive composition to the back of the paper or other hanging material and drying. The dried adhesive coating, when remoistened, was slow drying, had satisfactory slip characteristics and the pregummed material was otherwise very satisfactory for hanging purposes.

The term "cereal flour" is employed herein to cover the flours of cereal grains including, for example, wheat, oats, rye, rice, and barley. Those grains containing a substantial proportion of protein, and especially wheat and rye, are particularly suited for the practice of the invention. Hydrolized cereal flour is employed to cover a cereal flour which has been degraded or converted in the wet with acids and/or enzymes. The term "enzyme hydrolized cereal flour" is employed herein to cover hydrolized cereal flours which have been degraded or converted in the wet primarily due to the action of enzymes. In these enzyme conversions the pH may be adjusted and may be varied, depending upon the particular type of flour, the amount of enzyme present, and the amount of conversion desired.

In the practice of the invention with enzyme converted cereal flours, the enzyme may be a chemically isolated enzyme, as in Example IV, or more preferably is derived from a cereal flour having a predetermined minimum natural enzyme content, as for instance in Examples I and II, or from a blend of cereal flours, one of which

has a relatively high enzyme content, as for instance in Example V. In general, the alpha amylase content may be taken as a measure of enzyme activity in a cereal flour, and it is preferable for the purpose of the invention to employ a cereal flour or a blend of cereal flours having a predetermined alpha amylase content or a predetermined average alpha amylase content of at least 0.25 unit, as determined by the method of Kneen and Sandstedt, supra, preferably in excess of 0.4 unit. The maximum enzyme content is not so critical because it can be compensated for by adjusting the pH and still obtain the desired predetermined viscosity. Thus, with an enzyme content of say 0.43 unit, as in Example III, the pH is preferably within the range of about 6.5 to 7. If the enzyme content were much higher, it could be compensated for by adding an alkaline reacting substance to increase the pH and thereby reduce the enzyme activity.

The expressions "plasticizer" and "plasticizing agent" are used herein to cover any substance which, when incorporated with the adhesive, has the effect of slowing the rate of drying of the remoistened adhesive coating and also tends to reduce the curling tendency of the dried adhesive coating when applied to a flexible base material, such as paper. Any water soluble salt, such as sodium chloride, sodium formate, sodium sulphate, sodium acetate, sodium nitrate, sodium thiocyanate, and the corresponding potassium, calcium, and magnesium salts which are soluble are effective to slow down the rate of drying of the remoistened adhesive and to some extent prevent curling. Other plasticizing agents are more effective in reducing the tendency to curl, including for example, sodium lactate, urea, glycerine, glucose, invert sugar, and other hygroscopic substances. In many instances, therefore, it is preferable to employ a combination of plasticizing agents. As previously indicated, the reducing sugars formed by the hydrolization of the cereal flours also act as plasticizing agents and according to one method of practicing the invention a hydrolized cereal flour containing a large percentage of reducing sugars may be blended with a hydrolized cereal flour containing a smaller percentage of reducing sugars. Thus, a product such as that of Example II may be blended with one such as described in Example I. If the reducing sugars content is sufficiently high, the auxiliary plasticizing agent may be omitted or the amount of the auxiliary plasticizing agent may be substantially reduced. In general, it is preferable to have a minimum total plasticizing content of the dried adhesive, including the reducing sugars, in the hydrolyzed cereal flour of at least 10%. Ordinarily the maximum plasticizer content will not be greater than about 50% including the reducing sugars.

The adhesives employed in accordance with the invention may be prepared in the form of dry base materials comprising a cereal flour containing a predetermined natural enzyme content, as previously defined, or a blend of a cereal flour with another cereal flour having a natural enzyme content sufficient to produce said predetermined enzyme content or a cereal flour with a chemically isolated enzyme added thereto, or blends of cereal flours with other amylaceous materials including starches, in combination with an auxiliary plasticizing agent of the type previously mentioned preferably in an amount equal to at least 5% by weight of the total dry base and not greater than about 45% by weight. The dry base containing the plasticizer is then hydrolized to form the adhesive in the manner previously described and the latter is applied to the back of a hanging material to form a dried coating thereon. Bases of this type can also be used in making decalcomanias.

One of the advantages of the invention is that the specific type of adhesive base material employed not only gives a product of excellent adhesive characteristics for the purpose but also makes it possible to reduce, or in some cases, eliminate relatively expensive auxiliary plasticizing agents. Another advantage of the invention is that the adhesives and pregummed hanging materials prepared therewith are derived from readily available raw material and, as previously indicated, good results have been obtained by using sprout damaged grain which cannot ordinarily be employed for foods. Other advantages will be apparent to those skilled in the art.

Having thus described the invention, what we claim as new and desire to secure by Letters Patent of the United States is:

1. A pregummed hanging material comprising a base material having thereon a dried coating of an adhesive comprising as an adhesive base a hydrolyzed cereal flour having a reducing sugars content of at least 5% and not more than about 26% by weight of said dried coating calculated as dextrose, said adhesive coating when moistened possessing retack properties and slip characteristics permitting said material to slide while the adhesive is still wet after it is first applied to a surface.

2. A pregummed hanging material comprising a base material having thereon a dried coating of an adhesive comprising as the adhesive base a hydrolized cereal flour, said hydrolized flour being intimately associated with at least one auxiliary plasticizing agent, the reducing sugars content of said flour being such that said adhesive coating contains at least 5% and not more than about 26% by weight on a dry basis of reducing sugars calculated as dextrose and a minimum of 10% by weight of total plasticizer including reducing sugars, said plasticizer being effective to retard the rate of drying of said dried coating and to reduce the tendency of said coating to curl and said adhesive coating when moistened possessing retack properties and slip characteristics permitting said material to slide while the adhesive is still wet after it is first applied to a surface.

3. A pregummed hanging material comprising a base material having thereon a dried coating of an adhesive comprising as the adhesive base a hydrolized cereal flour, said hydrolized flour being intimately associated with at least one auxiliary plasticizing agent comprising a water soluble salt, the reducing sugars content of said flour being such that said adhesive coating contains at least 5% and not more than about 26% by weight on a dry basis of reducing sugars calculated as dextrose and a minimum of 10% by weight of total plasticizer including reducing sugars, said plasticizer being effective to retard the rate of drying of said dried coating and to reduce the tendency of said coating to curl and said adhesive coating when moistened possessing retack properties and slip characteristics permitting said material to slide while the adhesive is still wet after it is first applied to a surface.

4. A pregummed hanging material comprising a base material having thereon a dried coating of an adhesive comprising as the adhesive base

a plurality of hydrolized cereal flours, said hydrolized flours being intimately associated with at least one auxiliary plasticizing agent, the reducing sugars content of said flour being such that said adhesive coating contains at least 5% and not more than about 26% by weight on a dry basis of reducing sugars calculated as dextrose and a minimum of 10% by weight of total plasticizer including reducing sugars, said plasticizer being effective to retard the rate of drying of said dried coating and to reduce the tendency of said coating to curl and said adhesive coating when moistened possessing retack properties and slip characteristics permitting said material to slide while the adhesive is still wet after it is first applied to a surface.

5. A pregummed hanging material comprising a base material having thereon a dried coating of an adhesive comprising as an adhesive base a hydrolized cereal flour intimately associated with a plasticizing agent, the total amount of said plasticizing agent, including at least 5% reducing sugars calculated as dextrose present in said hydrolized cereal flour, being at least 10% by weight of the adhesive calculated on a dry basis and said adhesive when diluted with water to bring the ratio of solids to water to 1 part of solids to 10 parts of water having a viscosity between 15 centipoises and 750 centipoises at 75° F.

6. A pregummed hanging material comprising a flexible base material having thereon a dried coating of an adhesive comprising as the principal adhesive base a hydrolyzed cereal flour and containing at least 10% but not more than about 50% by weight on a dry basis of a plasticizer including a reducing sugars content of at least 5% by weight of said coating calculated as dextrose, the viscosity of said adhesive when diluted with water to bring the ratio of solids to water to 1 part of solids to 10 parts of water being between 15 centipoises and 750 centipoises at 75° F., and said adhesive coating when moistened possessing retack properties and slip characteristics permitting said material to slide while the adhesive is still wet after it is first applied to a surface.

7. A pregummed hanging material comprising a flexible base material having thereon a dried coating of an adhesive comprising as the principal adhesive base a hydrolized cereal flour and containing at least 10% but not more than about 50% by weight on a dry basis of a plasticizer including a reducing sugars content of at least 5% by weight of said coating calculated as dextrose, the viscosity of said adhesive when diluted with water to bring the ratio of solids to water to 1 part of solids to 10 parts of water being between about 16 to about 40 centipoises at 75° F., and said adhesive coating when moistened possessing retack properties and slip characteristics permitting said material to slide while the adhesive is still wet after it is first applied to a surface.

8. A pregummed hanging material comprising a flexible base material having thereon a dried coating of an adhesive comprising as the principal adhesive base an enzyme hydrolized cereal flour and containing at least 10% but not more than about 50% by weight on a dry basis of a plasticizer including a reducing sugars content of at least 5% by weight of said coating calculated as dextrose, the viscosity of said adhesive when diluted with water to bring the ratio of solids to water to 1 part of solids to 10 parts of water being between 15 centipoises and 750 centipoises at 75° F., and said adhesive coating when moistened possessing retack properties and slip characteristics permitting said material to slide while the adhesive is still wet after it is first applied to a surface.

9. A pregummed hanging material comprising a flexible base material having thereon a dried coating of an adhesive comprising a major proportion of a hydrolized rye flour and having a reducing sugars content of at least 5% by weight calculated on a dry basis as dextrose and a viscosity when diluted with water to bring the ratio of solids to water to 1 part of solids to 10 parts of water between 15 centipoises and 750 centipoises at 75° F., said adhesive coating when moistened possessing retack properties and slip characteristics permitting said material to slide while the adhesive is still wet after it is first applied to a surface.

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