Patented June 28, 1938

2,121,791

UNITED STATES PATENT OFFICE

2,121,791

CORK COMPOSITION AND METHOD OF MAKING

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No Drawing. Application September 14, 1934, Serial No. 744,094

3 Claims. (Cl. 106—22)

The present invention relates to cork composition and method of making same. By cork composition, is meant a composite cork structure formed predominantly of cork granules in closely compacted relation and which are held together by a binder. Such cork composition is prepared in the form of blocks, cylinders, sheets and in various shapes of either final commercial state or in form suitable for fabricating operations.

It is an important feature of the present invention, that the cork composition may be manufactured into the particular form or product by molding extruding, packing, rolling or sheeting. This is made possible by coating the granules with a binder which, in its unset or unhardened condition, does not interfere with the free flowing of the binder coated cork. Thus, the binder coated cork in contradistinction to a sticky agglomerate may be fed or piped in predetermined amounts, intermittently or continuously, from a suitable storage receptacle or from a hopper to the forming instrumentality.

The cork composition of the present invention possesses a light color comparable to natural cork and is characterized by possessing a maximum of cork properties. That is to say, the cork does not lose its identity and the product possesses enhanced compressibility and rebound. The cork composition of this invention is therefore resilient and is flexible and elastic and free of brittleness.

Cork composition is used in a variety of applications and is subjected to varying temperature conditions, moisture and not infrequently to chemical action. The present cork composition meets these requirements and is also acid and alkali resistant, resistant to mold growth, free of odor or odor contaminations, does not shrink or curl and possesses a long life.

In the manufacture of cork composition the margin of profit is small and any reduction in production costs is of substantial advantage. The present cork composition may be formed in an economic time cycle; that is, several operations including the making up of the binder, mixing with the cork, forming to shape and setting the binder to produce the final article are capable of accomplishment in a relatively short time period and with automatic apparatus.

In describing the cork composition and its method of manufacture, reference will be made to several embodiments which, for convenience, will be denominated (1) glue gel, (2) glue-glycerine gel, and (3) gel resin, the latter being a combination of either of the binders 1 and 2 with a resin, preferably a synthetic resin and forming the principal subject matter of this application.

Glue gel

By a glue gel, is meant a binder for the comminuted cork which comprises glue or gelatin and a solvent therefor, e. g., glycol with which is incorporated a hardening or tanning agent for the glue. In some cases I include a suitable wax.

In the manufacture of a binder of glue and glycol, there is used a suitable glue, such as bone or hide glue, and the same is placed in a closed jacketed kettle or other similar apparatus to which is also added a solvent, such as a polyhydric alcohol. Glycol, for example, diethylene or triethylene glycol or glycerine is a satisfactory alcohol. For example, glue and glycol are stirred to thoroughly mix them and, with or without continuing the agitation, the kettle and the mixture therein are heated to substantially 180° F. for about three hours in order to effect complete softening and solution of the glue. The proportion of glue to glycol can be varied but is preferably in the ratio of four parts of alcohol to one of glue. This ratio depends upon the strength and quality of the glue, since a strong glue may require as much as six parts of the solvent. As one example, four pounds of glycol and one pound of glue are mixed in the kettle and subjected to the heat treatment described. It is preferable not to go above 180° F., since I find that higher or sustained temperatures tend to deteriorate or destroy the glue base so that it loses its adhesiveness. The mixture is cooled to substantially 160° F. and drawn off at this temperature for admixture with the granulated cork.

The use of a polyhydric alcohol solvent has the further important function of providing a cork plasticizer, thereby enhancing the flexibility, elasticity and life of the cork composition.

A cork composition prepared from such a binder possesses a light color comparable to natural cork, a high tensile strength and is characteriezd by flexibility and a high degree of compressibility and rebound. This resilience of the cork composition is enhanced by the binder and, as heretofore stated, the cork properties are present in the cork composition in which the cork predominates by volume.

Glycol will eliminate the use of water as a solvent for the glue and therefore obviate one of the causes of shrinkage, curling and brittleness due to evaporation of water. The presence of the plasticizer, polyhydric alcohol will likewise render the cork composition substantially free of brittle-

ness. Again, the cork composition possesses hygroscopicity, which likewise insures continuous flexibility.

These are all very important characteristics and qualities of a product such as cork composition, which is used under a variety of conditions. For example, the cork composition of this invention is useful in the automobile industry for gaskets, window channels and in the closure industry as a liner material for caps for sealing certain kinds of medicines, chemicals and food products. Thus the cork composition is resistant to the action of moisture, heat and cold, alkalies and to weak acids. The tensile strength, resilience, flexibility and elasticity are properties which permit the cork composition to be compressed without danger of cracking or tearing under pressure.

Glue glycerine gel

By glue glycerine gel, is meant a binder wherein a portion or all of the glycol solvent is replaced by glycerine. I also include a suitable wax for certain compositions. Glycerine, I find, imparts a greater flexibility to the final cork composition and in addition to being a solvent for the glue is also a very satisfactory cork plasticizer. The glycerine is hygroscopic, giving continuous or greater life to the binder, so that brittleness is avoided, and all possibility of shrinkage is overcome. Instead of glycerine, I have used sulphonated castor oil or Turkey red oil.

In forming the gel solution in the kettle, the glycerine and glue are heated at 180° F. for one to three hours. Where the glycerine partially displaces the glycol, it is added to the kettle after the glue glycol solution has been heated at 180° F. for about two hours. Thereafter the solution of the three ingredients is continued at this temperature for approximately another hour before being drawn off. The steps previously described in the manufacture of the glycol glue gel cork composition are substantially followed.

The advantages and characteristics of the cork composition so produced are similar to those set forth for the glue gel cork composition. The product has improved flexibility and hygroscopicity and freedom from shrinkage, curling and brittleness. Again, the glycerine is a very efficient cork plasticizer and improves the life of the cork composition.

In forming a glue glycerine glycol cork composition, there is used for example, three pounds of glycol, two pounds of glycerine and one pound of glue. Six to eight pounds of glycerine are used where glycol is eliminated. The same hardening agents and in similar ratio will be used for curing the glue in the same manner as above described and the resultant solution will be added to the granulated cork in the ratio above indicated.

Resin-gel

By a resin-gel binder, is meant a binder including a gel solution of the order of those above described with which is combined a resin, preferably a synthetic resin, and which in some cases includes a suitable wax.

A very effective binder consists of either of the gel solutions already described, plus a suitable synthetic resin. The synthetic resins used are phenol formaldehyde resin of a fusible or infusible character, a urea aldehyde resin, a "Cumaron" resin or a "Glyptal" or alkyd resin. In fact, these resins may be combined to produce a binder having desired properties.

As one example, a glue gel solution is prepared as previously described and drawn off at a temperature of substantially 160° F. There is added to it a mixture of phenol formaldehyde resin and and urea formaldehyde resin in a suitable plasticizer solvent e. g., glycerine is prepared in accordance with the applications of Andrew Weisenburg, Serial Nos. 497,615, 497,616 and 675,636 owned by applicant's assignee.

The resin or resin solution in a partially cured state and at a temperature of about 140° F. is added to gel which is at substantially 160° F. It is important to keep the glue gel solution and the resin solution at temperatures low enough to prevent any premature reaction of the resin or any chemical effect upon the glue such as would cause it either to harden or deteriorate to lose its adhesive character. Thereafter, the binder formed of the mixture of gel solution and synthetic resin solution is mixed with a suitable hardener or accelerator for the resin, such as hexamethylenetetramine, oxalic acid and other organic acids as described in said Weisenburg applications. Preferably, the acid hardening agents are introduced in solution in a plasticizer solvent such as glycerine, glycol or sulphonated castor oil.

The binder is then mixed with the cork and the cork composition is formed immediately or stored as heretofore described.

It will be noted that no tanning or hardening agent for the glue is necessary where an acid hardener is used since free formaldehyde present by reason of the resin will serve this purpose. If, for any reason, there is insufficient of the hardener for the glue in the resin solution as prepared, one of the hardening agents above mentioned in suitable percentage will be added to tan the glue.

In preparing the binder, there is used, for example, two parts of the gel solution to one part of the resin, with a sufficient amount of oxalic acid or other hardening agent as will effect curing of the synthetic resin under a temperature of substantially 280° F. and the pressures employed in carrying out the molding or forming operation. The hardening agent in the case of oxalic and similar acids is preferably combined in equal parts with a solvent and cork plasticizer, e. g., glycerine, glycol or sulphonated castor oil and this solution is required in small percentage to harden or cure the resin. The temperatures of the oven may vary slightly and the time period also may be changed for effecting a curing of this resin gel binder, depending upon the type of resin employed and the particuluar hardening agent. The gel resin binder will be added to the comminuted cork in the ratio of about three pounds of binder to about twelve to thirteen pounds of comminuted cork.

The cork composition product has all of the advantages, characteristics, properties and uses of the cork compositions heretofore described and is acid proof and mold proof by reason of the presence of the resin. The cork composition will be utilized in the various applications heretofore described and, is useful for screw cap rings in Mason jars and as the cushion liner material for closure caps used in sealing foods such as pickles or products using a brine.

In referring to the Weisenburg applications, it will be understood that there is used any of the resins as well as mixtures of resins and proteins therein described. The various resins and resin mixtures set forth in the Weisenburg applica-

tions and equivalents all of which are utilized in forming the resin gel of this invention have not been specifically recited in this application in order that the specification may not be unduly prolix.

In addition to a cork composition having a resin gel comprising a phenol condensation product and a urea condensation product, there is also used other synthetic resins of the type above mentioned particularly a fusible phenol condensation product or a "Glyptal" or alkyd resin. Preferably, these are likewise incorporated with a suitable solvent or cork plasticizer and are in a partially or semi-cured state for admixture with the gel.

A resin gel using a phenol condensation product is prepared in the following manner:

A gel solution is prepared as previously described and drawn off at a temperature of about 140–160° F. There is then added to it a phenol formaldehyde condensation product prepared in the following manner.

A suitable mixture of phenol and formaldehyde solution together with oxalic acid, previously dissolved in enough water to form a solution, are mixed in a suitable vessel and heated slowly, preferably by means of steam until reaction starts. The steam is then shut off and the mixture is allowed to react for approximately twenty minutes in the heated vessel. Thereupon, cold water is run into the reaction product to cool the same and stop the reaction. The mass is permitted to settle for about forty-five minutes to one hour, so that the resin precipitates. The water is now siphoned off and therein is subsequently given several, i. e., about four, separate washes with water at a temperature of about 120° F. to remove the oxalic acid. In each case, the mass is permitted to settle for about twenty minutes to one-half hour and the water removed. The final product is now boiled under vacuum until the reaction product becomes clear, and substantially all remaining water is removed, and until the resin presents a viscous character having substantially the viscosity of a string. The resin is now preferably, but not necessarily, dissolved in a suitable plasticizer, for example, glycerine or glycol or sulphonated castor oil and is ready for admixture with the gel solution. The resin is in a partially cured state, and is preferably at a temperature of about 140° F. for admixture with the gel.

It is important to keep both the gel solution and the resin solution each at temperatures low enough to prevent any premature reaction or curing of the resin or any chemical effect upon the glue, such as would cause the adhesive base to deteriorate.

The resin or resin plasticizer solution having a temperature of substantially 140° F. is now mixed with the gel having a temperature of about 160° F., and, as stated, these temperatures are controlled to prevent any reaction of the glue or the resin. This mixing of the resin with the gel will preferably take place just prior to the addition of a hardening agent or accelerator for the resin. In the present instance, hexamethylenetetramine is used as the hardening agent and added to the binder. The binder at a temperature of about 140–160° F. is thereupon mixed with the cork and in the manner above described. The binder coated cork is either passed to the forming instrumentality or stored at a low temperature in a chilling room, as above mentioned.

In forming the cork composition, two pounds of gel and one pound of phenolic resin are mixed as described, and to this mixture is added four ounces of the hexamethylenetetramine solution for each three pounds of binder. The binder is incorporated with the comminuted cork in the ratio of three pounds of binder to substantially twelve to thirteen pounds of comminuted cork. These proportions are purely exemplary, but are substantially followed in preparing the cork composition on a commercial scale.

The cork composition has all of the advantages of the cork composition above described, and in employing hexamethylenetetramine as a curing agent for the resin, as well as the glue, there results a substantial saving in chemicals.

The binder coated cork in the several examples described is free flowing and it is to be noted that the resin, as well as the glue, is cured or set in the presence of the cork.

In all of the several embodiments, the cork composition is moisture or water proof and is not affected by heat and cold, notwithstanding that it is subjected to high pressure.

With respect to the adhesive for the gel, there is used both vegetable or animal glues and/or gelatins of various kinds and properties as desired, also albumen and casein; the term "glue" is therefore used throughout the specification as inclusive of all of these adhesives which are defined in the "Chemical Dictionary" by Hachk 1929.

While synthetic resins have been mentioned as preferred, natural resins are in a number of cases useful in lieu thereof. Thus resins such as the dammars and copals are employed. Mixtures of natural and synthetic resins sometimes are used.

In this specification, I have referred to glycerine, glycol and sulphonated castor oil as solvents and plasticizers. For beverage purposes and where taste and odor contaminations or effects must be safeguarded, glycerine is preferred. Glycol acts to dissolve cap lacquers and sulphonated castor oil imparts an undesirable odor. For all other purposes, however, the cork composition embodying any of the solvent plasticizers is satisfactory.

I have referred herein to the use in some cases of a binder including a wax which is melted and added (*a*) to the gel binder, (*b*) to the gel binder before mixing with the resin, (*c*) to the resin binder before admixture with the gel, and (*d*) to the gel-resin binder. This wax will have the required melting and hardening point for the intended cork composition and is of vegetable, animal or mineral origin. Paraffin, carnauba, beeswax, white and yellow wax, are examples of those employed. In the case of beverage cap liners, the wax will preferably be one imparting neither taste or odor to the cork composition. Again, the melting point of the wax will be selected in accordance with the use of the cork composition, i. e., the degree of heating to which the cork composition will be subjected. The wax in fluid condition will readily mix in most cases with the several binders and performs the function of a lubricant for the cork composition. This property is particularly true where the cork composition is extruded, the lubricant very materially aiding in the extruding operation, and is also assistive in the ordinary molding operation to overcome any possibility of sticking of the cork composition. Only a small percentage of wax is added to the binder, preferably an amount to

exert in the particular cork composition a lubricating function. The wax, as will be appreciated, has a binding action, stabilizes the cork composition, and enhances its chemical resistance and waterproofing.

When the wax employed is not readily miscible with the binder, a suitable wax carrier may be employed as understood in the art, e. g., a latex or rubber mixture will be used.

Likewise, I have referred herein to a number of hardening agents for both the glue and the resin. It will be understood that one of these will be used as desired, and that equivalents thereof will be employed wherever found useful.

The cork composition in accordance with this application consists of the cork which predominates by volume, and the binder; the binder is provided in a thin film upon the cork particles and the mixture compressed and compacted into various forms, the binder being cured either during the forming operation or subsequent thereto. That is to say, while I have referred to forming and then curing the mix in a travelling oven while the cork composition is confined in the forming instrumentality, the cork composition, where being extruded into rods or other shapes, will have the binder simultaneously cured concomitantly with the extruding operation, e. g., in the extrusion tube.

I have referred herein to resin gel mixtures and resin gel wax mixtures and in addition to the examples given, I form a very satisfactory cork composition useful as a liner in association with caps for the beverage, food, drug and general chemical field by using a urea resin gel or a "Glyptal" or alkyd resin gel. For example, I form a cork composition of comminuted cork, a urea resin and a gel of glue or gelatin preferably using glycerine, and in some cases incorporate with the same a suitable wax. Instead of using a urea resin I in some cases employ the alkyd resin and if desired for certain compositions a combination of urea and alkyd resins is employed.

All of the several cork compositions are useful for gaskets, window channels, and sealing liners for caps, and in fact may be utilized in all of the various applications of composition cork.

I claim:—

1. A cork composition consisting of cork granules, a polyhydric alcohol plasticizer, and a mixture of adhesives consisting of an adhesive selected from a group consisting of glue, albumen, and casein and an adhesive resin selected from a group consisting of dammars, copals, phenolic resins, cumaron resins, and alkyd resins, said adhesives being present in amount to constitute a binder for the cork granules and said comminuted cork predominating by volume.

2. A cork composition consisting of cork granules, a wax, a mixture of adhesives consisting of an adhesive selected from a group consisting of glue, albumen, and casein and an adhesive resin selected from a group consisting of dammars, copals, phenolic resins, cumaron resins, and alkyd resins, said adhesives being present in amount to constitute a binder for the cork granules and said comminuted cork predominating by volume.

3. A cork composition consisting of cork granules, a polyhydric alcohol plasticizer, a wax, a mixture of adhesives consisting of an adhesive selected from a group consisting of glue, albumen, and casein and an adhesive resin selected from a group consisting of dammars, copals, phenolic resins, cumaron resins, and alkyd resins, said adhesives being present in amount to constitute a binder for the cork granules and said comminuted cork predominating by volume.

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