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LOW SHRINKING CELLULOSIC REPAIR PUTTY

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This invention relates to organic plastic compositions and more particularly to plastic compositions containing an improved filler dispersed or uniformly distributed in a binder vehicle comprising an organic polymeric material.

Many plastic compositions containing various types of fillers have long been commercially available. So-called "plastic wood" products represent the most common type of plastic compositions which find manifold uses for general repair of wood and metal articles such as filling cracks or dents in such surfaces and for cold molding of objects. These products usually consist of a binding vehicle of nitrocellulose or certain synthetic resins dissolved in volatile solvents and containing wood flour as a filler and are of a dough-like consistency to facilitate their use for the stated purposes. When dried at room temperature, the volatile solvents are evaporated and the composition sets up to a hard dense mass resembling wood in many ways in that it may be drilled, sawed, planed and stained or painted in much the same manner as wood itself. However, these products have universally been characterized by a serious defect of excessive shrinkage which militates against many uses for which materials of this type would otherwise be suited. Many attempts have been made to overcome this defect but such efforts have met with little or no success. In compositions which make use of cellulose derivatives as the binder it has been proposed to employ a true solvent and diluent or non-solvent in carefully controlled and critical proportions to counteract shrinkage tendencies. A select class of synthetic resins has also been suggested as the vehicle for the commonly used wood flour filler as a means for overcoming shrinkage. In these and other known attempts to solve the shrinkage problem, only partial if any success has been achieved and then in some cases only at the sacrifice of some other equally important property.

This invention has as a primary object the provision of an organic plastic composition containing an inert, organic filler which is substantially free of shrinkage tendencies. Another object is the provision of an organic plastic which permits the inclusion of higher amounts of inert filler thus contributing substantial economies. Another object is the provision of a plastic composition containing high amounts of organic, inert filler which is more dense when dried than plastic compositions of this type heretofore available. Another object is the provision of a plastic composition which is more receptive to staining to give an appearance resembling that of wood. A further object is the provision of a plastic composition which is more readily sanded to a smooth surface. A further object is the provision of a plastic composition which may be drilled, machined, planed and otherwise mechanically treated in a manner similar to wood. A still further object is the provision of a plastic composition containing an inert, organic filler which is tough and resistant to warping and cracking. Other objects will appear as the description of the invention proceeds.

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These objects are accomplished in accordance with the present invention by means of a composition containing a finely divided, organic, inert material characterized by an oil absorption of less than about 175 dispersed or uniformly distributed in an organic polymeric binder in the proportion of between about 2.5 and 5 parts by weight of said inert material to 1 part by weight of binder.

The following examples are given by way of illustration only and no limitations are intended thereby except as indicated in the appended claims.

Example 1

	Per cent by weight
Cellulose nitrate [1]	14.0
Isobutyl acetate	16.4
Petroleum hydrocarbon (B. R. 88–131° C.)	2.0
Denatured alcohol (23A)	7.6
Isobutyl acetate	15.0
Dibutyl phthalate	5.0
Walnut shell flour	40.0
	100.0

[1] The cellulose nitrate used in this example had a viscosity characteristic of 5 seconds determined in accordance with A. S. T. M. specifications D–301–33, Formula C, and a nitrogen content of 12%.

The total solids content of the composition was 59.0% and the ratio of walnut shell flour to cellulose nitrate was 2.9 to 1 parts by weight.

The oil absorption characteristic of the walnut shell flour was 124.

In preparing the composition the cellulose nitrate was dissolved in the solvent vehicle of the first portion with an agitator mixer. The walnut shell flour was mixed in a kneading machine with the isobutyl acetate and dibutyl phthalate for about 4 hours after which the second portion was added to the first portion with mixing until a uniform homogeneous product was obtained.

The resulting plastic was placed in a bored-out hole ¾" in diameter and ¼" deep in a wood block with mild manual pressure and allowed to dry for 16 hours at room temperature. Adhesion to the walls of the hole was good and substantially

no shrinkage or breaking away from the walls of the hole was observed. The plastic was found to be hard and tough, easily sanded and readily stained to resemble the wood surface surrounding the plastic.

Example 2

	Per cent by weight
Polyvinyl butyral resin (high velocity)	11.0
Denatured alcohol (23A)	23.8
Isobutyl acetate	4.7
Isopropyl acetone	5.9
Denatured alcohol (23A)	13.6
Walnut shell flour	41.0
	100.0

The polyvinyl butyral resin of this example may be prepared by any of the methods well known in the art, for example, by treating polyvinyl acetate with a hydrolyzing agent such as sulfuric acid followed by condensation with butyraldehyde to give a solid fusible resin soluble in certain organic solvents. The hydroxyl content of the resin was about 10%. The viscosity of the resin was 440 centipoises determined in 10% concentration in a mixture of 54 parts by weight of denatured alcohol (23A) and 36 parts by weight of 99% ethyl acetate.

The total solids content of this example was 52.0% and the ratio of walnut shell flour to resin binder was 3.7 to 1 parts by weight.

The composition was prepared by dissolving the polyvinyl butyraldehyde resin in alcohol, followed by the addition of the solvents of the second portion as indicated and finally the walnut shell flour was incorporated by mixing until a homogeneous mass was obtained. This product when tested as in Example 1 gave results which indicated its usefulness as a "plastic wood" material.

Example 3

	Per cent by weight
Polyvinyl butyral resin (high velocity)	9.4
Denatured alcohol (23A)	20.1
Isobutyl acetate	4.0
Isopropyl acetone	5.0
Denatured alcohol (23A)	11.5
Walnut shell flour	50.0
	100.0

This example is similar to Example 2 except the total solids content was 59.4% and the ratio of walnut shell flour to resin binder was about 5.3 to 1 parts by weight. This composition was also found to be satisfactory as a "plastic wood" material.

Example 4

	Per cent by weight
Vinyl chloride-vinyl acetate copolymer	15.0
Methyl ethyl ketone	45.0
Walnut shell flour	40.0
	100.0

The vinyl resin used in this example consisted of a copolymer of vinyl chloride and vinyl acetate comprising the reaction product of about 85% vinyl chloride and about 15% vinyl acetate with an average molecular weight of 10,000.

The total solids of the composition was 55% and the ratio of walnut shell flour to vinyl resin copolymer was 2.7 to 1 parts by weight.

This example also represents a composition which was found to be suited for the purposes of the present invention.

Example 5

	Per cent by weight
Alkyd resin [1]	17.0
High solvency petroleum naphtha (B. R. 154–207° C.)	12.2
Apricot shell flour	53.8
High solvency petroleum naphtha (B. R. 95–135° C.)	17.0
	100.0

[1] The alkyd resin used in this example was a 50.0% linseed oil modified diglycerol triphthalate resin.

The total solids of this composition is 70.8% by weight and the ratio of resin binder to apricot shell flour is about 3:1 parts by weight.

The apricot shell flour was incorporated in the alkyd resin solution by mixing until homogeneous after which the high solvency petroleum naphtha with a boiling range of 95–135° C. was added with mixing to provide a dough-like consistency suitable for the designated use of the product.

When tested as in Example 1, this product was found to give excellent results as a "plastic wood" with properties similar to those of the preceding compositions.

Example 6

	Per cent by weight
N-butyl methacrylate resin polymer	15.2
High solvency petroleum naphtha (B. R. 95–135° C.)	17.8
Butyl acetate	2.0
Walnut shell flour	55.0
High solvency petroleum naphtha (B. R. 95–135° C.)	10.0
	100.0

This composition was prepared in accordance with the procedure described for Example 5.

The total solids content of this composition is 70.2% by weight and the ratio of methacrylate resin binder to walnut shell flour is 3.6:1 parts by weight.

As in the preceding examples, this product when tested as a "plastic wood" filler by forcing the material into a hole bored in a wood panel and drying gave a hard, tough, substantially non-shrinking plastic on drying that was eminently suited for general repair or filler purposes for wood objects or for molding work.

Example 7

	Per cent by weight
Cellulose nitrate (low viscosity) [1]	5.6
Polyvinyl butyral resin	7.4
Dibutyl phthalate	1.0
Walnut shell flour	24.0
Redwood flour	16.0
Denatured alcohol (23A)	28.1
Isobutyl acetate	9.7
Isopropyl acetone	3.9
Ethyl acetate	3.5
Petroleum hydrocarbon (B. R. 88°–131° C.)	0.8
	100.0

[1] The cellulose nitrate used in this example had a viscosity characteristic of 6 seconds determined in accordance with A. S. T. M. specifications D–301–33, Formula C, and a nitrogen content of 12%.

The polyvinyl butyral resin of this example was of the same type as that described in Example 2.

The total solids content of the composition was 54.0% and the ratio of filler to organic polymeric binder (cellulose nitrate and polyvinyl butyral resin) is about 3:1.

The oil absorption of the composite filler consisting of walnut shell flour (oil absorption—124) and Redwood flour (oil absorption—258) in the proportions shown is 156. It will be noted that these fillers are present in the proportion of 3 parts by weight of walnut shell flour to 2 parts by weight of Redwood flour illustrating that some filler of oil absorption greater than 175 may be used. However, in all cases, for the present invention, the content of the high oil absorption filler must not exceed that amount which, when combined with a low oil absorption filler, will give a resultant oil absorption greater than about 175, that is, the oil absorption of the composite filler must always be less than about 175.

The composition of Example 7 was prepared by dissolving the cellulose nitrate and polyvinyl butyral resin separately in a portion of the solvents and diluents in a conventional manner followed by charging the solutions into a kneading machine and then adding the remainder of the solvents, plasticizer and filler while kneading the mixture in a masticating machine such as a Werner & Pfleiderer mixer until a homogeneous mass was secured.

When tested as in Example 1, this product was found to give excellent results as a "plastic wood" with properties similar to those of the preceding compositions.

The examples illustrate a number of types of organic polymeric materials which may be employed as binder vehicles for the organic, inert filling material. In general, organic polymeric materials which are soluble in volatile organic solvents and which are capable of hardening with or without the addition of suitable catalysts to tough, water-resistant plastics upon evaporation of the volatile solvents or on a short aging thereafter and which do not substantially change in physical or chemical properties over extended periods in the stated uses are suited for the present invention. Organic polymeric materials in addition to those given in the examples include cellulose acetate, mixed cellulose esters such as cellulose acetobutyrate, phenolic, urea and melamine type resins, alkyd resins, other vinyl type resins including styrene, partially hydrolyzed polyvinyl acetate combined with a styrene-maleic anhydride interpolymer such as described in co-pending application to Blyler et al., Serial No. 494,266 filed July 10, 1943, now Patent No. 2,419,880, April 29, 1947, polythene resins and soluble nylon resins preferably N-alkoxy-methyl polyamides such as described in co-pending application to John D. Pickens, Serial No. 529,832 filed on even date herewith and various mixtures or blends of these polymeric materials.

As previously indicated, the filler employed with the organic polymeric binder material consists of finely divided, inert, organic material, preferably a cellulosic material, characterized by an oil absorption of not more than about 175 and preferably less than about 150. Suitable materials include walnut shell flour (oil absorption 115; or one having an oil absorption of 124), apricot shell flour (oil absorption 76), and finely ground regenerated cellulose (oil absorption 78). Conventional wood flour, specially treated by ball mill grinding for about 18 to 36 hours to compact its structure and reduce its oil absorption to about 139 is also satisfactory. Redwood flour or Redwood plastic pulp when similarly treated to reduce the oil absorption to 92 and 52, respectively, are particularly useful. Conventional wood flour which is merely comminuted to small particles and not ground so as to compact its structure as indicated above has an oil absorption of 319 and is not satisfactory. Oil absorption determinations were made in accordance with the standard "Rub-out" method described in "Physical and Chemical Examination of Paints, Varnishes and Lacquers"—H. A. Gardner, 1939, p. 209.

The plastic compositions of the invention may comprise the organic, polymeric binder material and the inert, organic filler in the proportion of between about 2.5 and about 5 parts by weight of inert filler to 1 part of polymeric binder. If the proportion of polymeric binder is substantially less than 2.5 parts to 1 of binder, the consistency of the product is too low for proper handling and working. In addition, there is a greater tendency toward shrinkage and the product becomes more resinous in character losing its resemblance to wood in appearance and working properties. If the proportion of binder to inert filler is substantially greater than 5 to 1, the final product on drying becomes crumbly and is not sufficiently tough for the present purposes.

With the new fillers a higher total solids content in the plastic composition is permitted and whereas in compositions of this type heretofore available, the total solids content is substantially less than 50%, best results are obtained in the new products where the solids content is more than 50%.

Plasticizers or softeners may be included in the improved "pastic wood" compositions but the amount should be limited so as to maintain the wood-like properties of the preferred compositions. In some instances, in order to aid in converting certain resin polymers to the infusible, insoluble state the addition of catalysts in such proportions as will promote the reaction is contemplated. Also, for some resin polymers, for example, polyvinyl butyral resins, particularly if the use of the plastic compositions of the invention provides for moderate heating, it may be desirable to add a small amount of a cross-linking agent such as stearato chromic chloride or acetate described in my co-pending application Serial No. 498,981, filed August 17, 1943, now Patent No. 2,410,414, November 5, 1946, to insolubilize and raise the softening point of the resin polymer.

The volatile solvents are not critical except that proper solvents should be selected for each specific type of polymeric binder. The evaporation rate may be varied considerably depending upon whether a very rapid drying composition is used when the solvents should have a fairly high evaporation rate or whether the products should dry slower for certain uses where longer period of workable consistency is required in which case the solvent vehicle should be adjusted to have a lower evaporation rate. However, it is preferred to keep the solvent portion in an amount less than 50% of the total composition.

As previously indicated, the new products are receptive to conventional stains and when so treated give an appearance closely resembling stained wood. The stain may be applied to the

surface after the plastic composition has hardened or it may be incorporated in the composition as a part thereof. The new products may also be pigmented with ordinary pigment materials by the addition of such coloring matter with mixing or other conventional processing to afford uniform distribution of the coloring matter.

The uses of the products of the invention are many and varied. An important and primary utility resides in repair work in wood such as furniture and the like where the new compositions may be employed for filling cracks, screw and nail holes, surface imperfections and joints. The products may be used for cold-molding and for filling dents and imperfections in metal surfaces.

The new compositions are characterized by numerous advantages. Of primary importance is the substantial elimination of shrinkage in the products which thereby avoids cracking, warping and breaking away from the surfaces with which the composition is in contact. Greater amounts of inert filler are permitted in the present compositions, thus contributing important economies. Improvements in staining are also apparent and the appearance and working propertien of the hardened material are unusually similar to those of wood. The products show improvements in sanding properties and may be sawed, drilled, cut, planed and in general worked mechanically in much the same manner as wood. The new plastic hardens rapidly at room temperatures, is unaffected by exposure to moderate heating and is highly resistant to water.

As many apparently widely different embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that I do not limit myself to the specific embodiments thereof except as indicated in the appended claims.

I claim:

1. A plastic composition prepared by blending without heating and adapted to harden on exposure to air at 70° F. without substantial shrinkage upon the evaporation of solvent which comprises a water-insoluble tough film-forming synthetic organic polymeric binder, a volatile solvent for the binder and a finely divided inert form of cellulose material characterized by an oil absorption of between 50 and 150 uniformly dispersed in the said binder in a proportion between 2.5 and 5.3 parts by weight of inert cellulose material to 1 part of the said organic polymeric binder, the said volatile solvent being present in amount from 29.2% to 50% of the total composition.

2. The composition of claim 1 in which the cellulose material is walnut shell flour.

3. The composition of claim 1 in which the cellulose material is ground Redwood flour.

4. The composition of claim 1 in which the organic polymeric binder is a vinyl resin.

5. The composition of claim 1 in which the binder is cellulose nitrate.

6. The composition of claim 1 in which the organic polymeric binder is a polyvinyl butyral resin.

7. The composition of claim 1 in which the ratio of inert cellulose material to organic polymeric binder is 3 to 1 by weight.

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