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VARNISHED SHEET MATERIAL

Henry A. Letteron, Schenectady, N. Y., assignor
to General Electric Company, a corporation of
New York

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1 Claim. (Cl. 117-161)

This invention relates to varnished sheet materials and more particularly is concerned with flexible sheet materials, for example cloth, paper, etc., varnished with an oil-modified alkyd resin (polyhydric alcohol-polybasic acid resin) the oily component of which is present in excess of 50 per cent by weight and which has an iodine number not exceeding 90.

One of the very important qualities of varnished cloth and similar varnished materials is the maintenance of flexibility even after prolonged exposure to elevated temperatures. Previous attempts have been made to prepare these sheet materials varnished with flexible alkyd resin compositions but they have been deficient in age-resistance characteristics, tending to lose flexibility and to become hard and brittle on prolonged standing, especially at elevated temperatures. Alkyd resins modified with minor portions of non-drying oils have been known but, so far as I am aware, the use of these resins has been limited to their incorporation into coating compositions such as nitrocellulose and urea-formaldehyde coating compositions. In such cases the alkyd resin is used merely to improve the plasticity and adhesive properties of the composition.

I have discovered that certain alkyd resins modified with at least 50 per cent by weight of fatty oils or fatty acids of low iodine number, for example non-drying oils and fatty acids thereof, will form dry, strong, tough, adhesive films under heat or, in certain cases, even at room temperature in the absence of other modifying resins or the like. This is surprising, since it is contrary to the theories of oil-drying reactions and to previous experience in varnish making from oils alone or from mixtures of oils and resins such as rosin, copal, etc. For a given oil length, I have observed that the rigidity of such oil-modified alkyd resins is greatly decreased by the presence of low-iodine number oils. The final rigidity is attained after a comparatively short bake and it remains practically unchanged even after remarkably long exposure to elevated temperatures.

These observations and discoveries led to my further discovery that varnished sheet materials, for example varnished cambric, silk, paper, metal foils, etc., having outstanding resistance to heat and aging can be produced by varnishing the sheet material with a varnish the base or primary component of which is composed essentially of the resinous reaction product of polyhydric alcohol, polybasic carboxylic acid and a major portion of a fatty substance the iodine number of which does not exceed 90. A fatty substance of such iodine number yields a modified alkyd resin film that remains flexible even after long exposure to high temperature and although the

amount of fatty substance is in excess of 50 per cent by weight of the resin, nevertheless tough films of high film strength are obtained.

The fatty substance may be a fatty oil, a fatty acid, specifically a fatty oil acid, or mixture of fatty oil and fatty acid, the individual oil or acid having an iodine number not higher than 90. Mixtures of different fatty oils or mixtures of different fatty acids, which oils or acids have an iodine number of 90 or lower, may be used if desired; or, the fatty substance may be a mixture of fatty materials having an iodine number higher than 90 with a different fatty material below 90 in iodine number, the proportions being so adjusted that the iodine number of the mixed fatty materials does not exceed 90. Such a mixture of fatty materials may be mixed fatty oils of high and low iodine number or mixed fatty acids of high and low iodine number; or, it may be a mixture of fatty oil or oils of high iodine number with a fatty acid or acids of low iodine number, or a mixture of high iodine number fatty acid or acids with a low iodine number fatty oil or oils.

In most cases I use an alkyd resin modified with from 50 to 85 per cent by weight of a fatty oil, preferably from 60 to 70 per cent, having an iodine number somewhat less than 90, for example about 85 to 88 as the upper limit. In certain cases fatty substances having little, if any, unsaturation may be employed, but ordinarily I do not use alkyd resins modified with fatty substance having an iodine number much less than about 5.

The varnished, flexible sheet materials of this invention have exceptional resistance to aging both at normal and at elevated temperatures. These remarkable aging properties are obtained without decreasing the toughness of the resin film or lengthening the baking cycle. The coated materials are smooth-surfaced and have excellent resistance to oil, moisture and abrasion. The resin film is hard, flexible, tough, pale in color, and has much less odor than the usual alkyd resin films.

In order that those skilled in this art better may understand how the present invention may be carried into effect, the following specific examples are given for purpose of illustration:

Example 1

	Parts by weight
Cocoanut oil	59.5
Glycerol	16.6
Maleic anhydride	23.6
Calcium oxide	0.3

The oil, glycerol and lime (esterification catalyst) are placed in a kettle equipped with a reflux condenser and stirrer and heated to approximately 250° C. for about 1 hour. The tempera-

ture is allowed to drop to about 190° C. and the maleic anhydride added. Cooking is continued until an acid number of about 8 is reached. The resulting resin is dissolved in a suitable solvent, for example petroleum spirits, in ratios such as to yield a varnish of the desired viscosity. Usually the varnish contains from about 50 to 70 per cent by weight of solids. Driers are added and the resulting varnish is applied to cloth or other flexible material in accordance with conventional practice. The coated article is usually baked to harden the coating.

Example 2

	Parts by weight
Soya bean oil fatty acids.....	26.5
Cocoonut oil fatty acids.....	25.7
Pentaerythritol.....	24.2
Phthalic anhydride.....	23.6

All the ingredients are placed in a kettle and heated for one hour at approximately 190° to 200° C. The temperature is raised to about 235° to 250° C. and cooking continued until a resin with an acid number of about 3 to 5 is obtained. The finished resin is handled in the same manner as described under Example 1.

Example 3

	Parts by weight
Cocoonut oil fatty acids.....	51.3
Pentaerythritol.....	21.9
Phthalic anhydride.....	25.6
Maleic anhydride.....	1.2

All the ingredients except the maleic anhydride are placed in a kettle and heated at approximately 190° to 200° C. until a clear pill is produced. The maleic anhydride is added and cooking is continued at approximately 235° to 250° C. until a resin having an acid number of about 5 to 8 is obtained. Varnishes and coated fabrics, metal foils, etc., are made from this resin in substantially the same manner as described under Example 1.

One unexpected result from the use of resins such as herein described in the production of varnishes and varnished materials is the improvement in film-forming properties which are obtained. For example, a non-drying oil such as cocoonut oil having incorporated therein a metallic drier may be spread into a film and held for four days at 150° C. without solidifying. In marked contrast a resin such as described under Example 1, with which has been mixed a small amount of a suitable drier, will form a solid non-tacky film upon being heated for less than one hour at 150° C.

Another unexpected result is the rapidity with which the herein-described resins may be converted to solid films at elevated temperatures. Textile materials such as cotton, wool, linen, silk, glass fibers, synthetic fibers such as superpolyamide fibers, etc., in woven, felted or other form, therefore can be coated or coated and impregnated with varnishes produced as set forth under the illustrative examples, and the applied film quickly solidified under heat to a hard, tough, moisture- and abrasion-resistant, substantially permanently flexible coating. Also, by suitable selection of oils and driers in producing the resin and varnish, resin films having air-drying properties may be obtained.

It is of course understood that the present invention is not limited to the production of sheet materials varnished with resinous compositions formed of the specific ingredients named in the

illustrative examples. For instance, other polybasic carboxylic acids or anhydrides may be used in forming the alkyd resin, in addition to those mentioned above and in lieu of, or in addition to, the polyhydric alcohols, glycerol and pentaerythritol, named in the illustrative examples, I may use similar polyhydric alcohols.

As illustrative of fatty oils and fatty acids which, as commercially available, usually have iodine numbers of 90 or less and which may be used alone or mixed in producing the oil-modified alkyd resins employed in carrying the present invention into effect, I mention the following commonly classified as vegetable fats:

	Approximate iodine number of—	
	Oil	Fatty acids
Cocoonut.....	5-10	6-10
Palm kernel.....	8	12
Palm.....	49-59	53
Cottonseed stearin (gossypium).....	86-90	90

It will be understood by those skilled in the art that the iodine numbers of the oils and fatty acids mentioned above may vary somewhat, depending, for example, upon the particular source of the raw material and the extent to which the material has been purified. The fatty oils and fatty acids used in producing the hereindescribed oil-modified alkyd resins are bought on specification, the acceptable fatty substances in all cases having an iodine number not exceeding 90.

Of the above mentioned commercially available fatty oils and fatty acids, known as vegetable fats, the cocoonut oil or acids form varnished sheet materials which are outstanding in their flexibility and lack of odor while the cottonseed stearin is preferred from the cost standpoint. Those cottonseed products of this type so prepared as to have an iodine value below 90 are used. When a single oil or acid is used, the cottonseed stearin is highly satisfactory for accomplishing the purposes of this invention. The resins prepared from all of the above vegetable fats give comparatively odorless films.

A suitable resin for making a varnish and varnished sheet material of superaging characteristics also may be produced by incorporating into the resin low-iodine-number fatty oils and (or) fatty acids, such as above mentioned, admixed with fatty oils and (or) fatty acids having an iodine number materially over 100, examples of which latter are:

	Approximate iodine number of—	
	Oil	Fatty acids
Soya.....	122-134	115-140
Walnut.....	132-152	150
Tung.....	163-171	144-159
Linseed.....	170-204	179-192
Perilla.....	185-200	200-211
Castor oil (dehydrated).....	About 135	About 145

In all cases the proportions of fatty materials of high and low iodine number are so adjusted that the iodine number of the mixture does not exceed 90. The dehydrated castor oil is to be distinguished from ordinary castor oil. The latter, frequently used in alkyd resin modification,

readily dehydrates during resin formation to form the more unsaturated product.

The method of combining the components of the resin may be varied in many ways, as is now well understood in the alkyd resin art.

In making the varnish the resinous composition may be thinned with any suitable solvent, for example turpentine, coal tar solvents, petroleum hydrocarbon solvents, etc. Any suitable drier and in any convenient form may be used, for example, the naphthenates, linoleates or resinates of metals such as calcium, manganese, lead, cobalt, zinc and iron. The percentage of drier required may be varied to suit manufacturing requirements for producing dry varnished sheet material in a minimum of time. Or, in some cases, the drier may be omitted. If desired, dyes may be incorporated into the resin or into the varnish in order to obtain transparent colored film. Also, if desired, the usual paint pigments may be introduced into the resin, as by grinding the components together, to form compositions yielding opaque, colored films of good flexibility.

The liquid coating composition or varnish is applied to the sheet material to be coated by brushing, sprinkling, spraying or, preferably, by immersion means and under temperature and other conditions commonly employed. Upon heating the varnished sheet material at a temperature of about 110° C. or thereabove, the solvent is evaporated and a varnished article of exceptional aging characteristics, good slip, and with a hard, tough, adhering resin film thereon is obtained.

In testing the heat and age resistance of the varnished sheet material a sample of the same is heated in a suitable oven at a temperature of about 125° C. The heated sample is tested for cracking of the resin film at the end of varying periods of time. This is done by wrapping the sample around a mandrel of suitable size, for example, 0.048 inch in diameter, and noting whether or not the resin film has cracked.

As illustrative of the way the resistance to aging is affected by the iodine number of the fatty substance used in the preparation of the resin, the following data are given:

Type of oil	Iodine number	Hours varnished cloth was heated at 125° C. before resin film cracked when cloth was wrapped around 0.048 inch mandrel
Series 1:		
(a) Soya bean oil fatty acids.....	130	72
(b) Cottonseed oil fatty acids.....	90	240
Series 2:		
(a) Cottonseed oil fatty acids.....	90	168
(b) Mixture of fatty acids of coconut oil and soya bean oil.....	70	720

The series 1 resins were prepared from

	Parts by weight	
	(a)	(b)
Soya bean oil fatty acids.....	71	---
Cottonseed oil fatty acids.....	---	71
Pentaerythritol.....	16	16
Phthalic anhydride.....	9	9
Maleic anhydride.....	4	4

The series 2 resins were prepared from

	Parts by weight	
	(a)	(b)
Cottonseed oil fatty acids.....	62	---
Soya bean oil fatty acids.....	---	31
Cocconut oil fatty acids.....	---	30
Pentaerythritol.....	18	20
Phthalic anhydride.....	18	10
Maleic anhydride.....	2	9

Resins of the type herein described are particularly useful in the preparation of materials such as the so-called "oiled silk" where extreme flexibility over a long time is required, together with toughness of film, light color and freedom from odor. Silk treated with the described coating compositions is especially suitable for use as covers for umbrellas, in the manufacture of raincoats, as covers for food containers, and for many other applications. The pigmented varnishes also may be used in the manufacture of so-called "oil cloth," "patent leather," and other articles where pigmented materials having characteristics comparable with those required in varnishes used in producing "oiled silk" are required. Certain of the varnished fabrics of this invention are particularly adapted for use in tape, sheet or other form as insulation for electrical conductors. In this connection reference is made to the copending application of J. R. Patterson, J. R. Reid and H. A. Letteron, Serial No. 306,520, filed concurrently herewith and assigned to the same assignee as the present invention.

The term "acid" as used broadly in the appended claim is intended to include within its meaning the anhydride of the acid.

What I claim as new and desire to secure by Letters Patent of the United States is:

A flexible, odorless, heat- and age-resistant, varnished fabric material consisting of fabric material coated and impregnated with a baked film of a composition composed of a polyhydric alcohol containing at least three hydroxyl groups, a mixture of phthalic anhydride and maleic anhydride, and 60-70 per cent by weight of cottonseed stearin having an iodine number below 90.

HENRY A. LETTERON.