United States Patent Office 3,013,895 Patented Dec. 19, 1961

3,013,895

QUICK DRYING VEHICLE AND METHOD OF DRYING SAME

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No Drawing. Filed Nov. 26, 1958, Ser. No. 776,450
14 Claims. (Cl. 117—38)

This invention relates to the art of coating materials. It has particular reference to an improved quick-drying vehicle for various coatings and to an improved method for rapidly indurating or drying such a vehicle after the coating operation.

The term coating materials is intended to cover vehicles or materials which embrace the characteristics of the subject invention and which may have applications in fields other than those specifically mentioned herein, such as, for example, photosensitive resists for use in the graphic arts, plugging materials for use in the drilling operations encountered in the petroleum industries, and the like. However, for illustrative purposes, and with no intent to limit its field of use, the invention will be described with particular reference to printing, wherein the coat-forming material is applied by a conventional printing plate.

Printing inks as made heretofore consist mainly of a non-aqueous vehicle, namely a drying oil, pigmented to the desired color. The drying oils commonly used for printing inks, such as tung oil, linseed oil, rape seed oil, dehydrated castor oil and alkyds, have by nature a drying rate which is slow compared to the potential operating speeds of printing presses, even when the usual driers (e.g. cobalt) are added to the oils. Particularly with the advent of the higher speed presses and multiple color printing, the avoidance of smudges and off-set on the successive sheets coming from the printing press has presented a serious problem.

Numerous attempts have been made to solve this problem. For example, the use of heat-set inks and steam-set inks, which were developed for this purpose, require the addition of large and expensive accessory equipment to the printing press in order to utilize the full productivity of the press; and the heat or steam tend to impair the dimensional stability of the paper and therefore the quality of the finished printed matter. The use of fine powder sprays or a transparent protective coating over the freshly printed surface (see Costell Patent No. 2,696,168, dated December 7, 1954) also requires considerable accessory equipment and is generally inconvenient.

It has also been proposed to increase the drying rate of printing inks by employing a catalyst or polymerization promoter in conjunction with heat or radiation of certain light energy. These proposals likewise involve objectionable features which have barred or greatly limited their commercial use. For example, a printing ink containing a diacyl peroxide as the catalyst will undergo skinning and livering even after a short period of storage under ordinary conditions, due to the strong oxidizing effect of this peroxide on the eleostearin of the drying oil, as disclosed in Hooft Patent No. 2,109,774 dated March 1, 1938. Thus, Hooft proposed to apply the diacyl peroxide to the paper separately from the ink,

which entails obvious disadvantages in commercial printing. Wendt Patents Nos. 2,453,769 and 2,453,770 disclose printing inks containing certain methane derivatives for promoting polymerization of the drying oil, and irradiation of the printed material with ultra violet light of certain wave lengths; but this expedient is admittedly unsuitable when a heat bodied tung oil is used as the vehicle and the use of pure eleostearin as suggested by Wendt will obviously result in an unstable product having too short a shelf life for commercial purposes.

The vehicles described in copending applications, Ser. Nos. 557,865, 562,671 and 563,423, are a substantial improvement over the prior art drying oil compositions. However, they are limited to drying periods of about two seconds. Modern presses can operate at rates requiring a printing ink vehicle that will not smudge within a fraction of a second after application.

The principal object of the present invention is to provide a quick-drying vehicle and a method for rapidly indurating or drying such a vehicle. Another object is to provide a quick-drying printing ink and printing method which enable a printing press to operate at extremely rapid speeds with no smudging or off-setting on the successively printed sheets, and without impairing the dimensional stability of the paper. Further objects are to provide a quick-drying ink containing a polymerization promoter which may be activated by ultra-violet light, alpha rays, or other forms of cold energy, and to provide an ink of this character which is stable in that it can be stored for a long period of time under ordinary conditions without livering. (While I have referred in the above to sheet-fed presses, it will be understood that the invention is also applicable to web-fed presses.)

By a quick-drying vehicle, I mean a vehicle which, when applied in a thin film of about two to four microns in thickness, as in printing, will dry or set rapidly. For example, Table I shows several of the compositions of this invention drying or setting in a fraction of a second; that is, the surface of the film when irradiated with cold energy, preferably ultra-violet light, becomes sufficiently dry so that in the case of a printing ink, for example, it will not off-set on succeeding sheets coming from the press. However, the drying action does not stop after the ultra-violet or activating energy is removed. On the contrary, in the practice of the present invention we have found that within a period of up to about 1.0 second after such removal of the activating energy, the polymerization or drying action has penetrated the entire film to provide a film which is hard throughout.

The quick-drying vehicle of the present invention consists essentially of any unsaturated polyester, any vinyl type monomer such as, for example, styrene, and any titanium ortho ester. I have found that compositions comprising the above named groups of compounds will yield, upon irradiation with ultra-violet light for a period of less than a second, a coating that will not offset or smudge. I have further found that these new vehicles will not liver or skin upon standing. In other words, these vehicles have good shelf life.

I have also found that unsaturated polyesters and drying oils which are normally incompatible are made miscible in the presence of an organic titanate, so that the vehicle may comprise a substantial amount of drying oil.

The reason for the extremely quick-drying property of

compositions containing an unsaturated polyester, a vinyl-type monomer and a titanium ortho ester is not entirely clear. It is suspected that the vinyl monomer attaches through addition type polymerization to the unsaturated bonds of the polyester to cause cross-linking. The role that the titanate plays in bringing about the desired coating is obscure, but without the titanate ester the quick-drying characteristic of the vehicle is absent.

The unsaturated polyester may be made by the esterification of a polyhydric alcohol and a polybasic acid, one or both of which contains a double bonded pair of carbon atoms, the double bond rendering the polyester capable of subsequent cross-linking. The unsaturated polyester is usually blended with a reactive cross-linking monomer, such as styrene, so that the mass upon being subject to polymerization condition forms a thermosetting resin.

The polyhydric alcohols most commonly used are glycols of ethylene, propylene, 1,3-2,3-butylene, diethylene and dipropylene. Unsaturated dihydric alcohols are presently not readily available; therefore, the double bond is generally supplied by the dibasic acid. Acids such as maleic anhydride and fumaric acid are satisfactory.

Suitable monomers are styrene, vinyl toluene, methyl methacrylate, or admixtures of these monomers with either diallyl phthalate or triallyl cyanurate.

The viscosity of the polyester-monomer composition should be such that the vehicle will spread and flow relatively easily. Viscosities of 2000–4000 centipoises have been found satisfactory. The vinyl monomer is preferably present to the extent of about 10–70% of the polyester.

Example of suitable organic titanates are tetraisopropyltitanate, tetra-n-butyltitanate, tetra 2-ethylhexyltitanate and tetra stearyltitanate. The titanate should be present in about the proportion of 0.2 to 1.5 parts of titanate per part of polyester, with a preferred range of 0.4 to 0.8.

The ultra-violet light used to trigger the polymerization reaction is preferably the full spectrum of ultra-violet, including 1800 A. to 4000 A., as we have found that isolated bands of the spectrum do not provide as rapid a polymerization as the full spectrum. An example of such a light source is a high pressure electronic discharge quartz mercury arc tube having an active length of about 1½ inches and drawing about 100 watts, the ultra-violet intensity of radiations of 3130 A. and shorter, measured at 20 inches distance, being over 250 microwatts per square centimeter.

The method of the invention comprises essentially the rapid induration of the vehicle by (1) forming a solution of the polyester, monomer and titanate, (2) forming a film of the resulting solution, and (3) irradiating the film with cold energy (preferaby ultra-violet light).

It is to be understood that in the practice of this invention the desired pigment may be added to the vehicle. Likewise, materials imparting a better press stability characteristic to the vehicle may be added without materially affecting the drying time. Examples of suitable stabilizing materials are chlorinated paraffin wax, ethylene glycol dibenzoate, N-methyl morpholine and methyl cellosolve acetate.

In the preferred practice of this invention, the vehicle containing the pigment in the desired proportion is applied in any suntable manner as a film to the material to be coated, such as a paper, and is then irradiated with the ultra-violet light to trigger the polymerization reaction.

When preparing the vehicle of this invention, it is preferable to add the organic titanate to the unsaturated polyester containing the monomer. Upon first adding the titanate a thick, gelatinous, sticky mass results. Allowing this mass to stand overnight results in the formation of a clear liquid. The formation of the clear liquid may be hastened by agitation.

Table I shows the drying times of vehicles of this invention when a thin film of the vehicle is irradiated.

Table I

	Vehicle	Percent by Wt.	Drying Time, Seconds
I.	Polyester	61.5	0.003
	Styrene	20.5	
	Sec.-Butyltitanate	18.0	
II.	Polyester	48.0	0.003
	Styrene	32.0	
	Sec.-Butyltitanate	20.0	
III.	Polyester	54.0	0.003
	Styrene	36.0	
	Sec.-Butyltitanate	10.0	
IV.	Polyester	60.0	0.003
	Styrene	15.0	
	Sec.-Butyltitanate	25.0	
V.	Polyester	36.0	0.003
	Styrene	24.0	
	Sec.-Butyltitanate	40.0	
VI.	Polyester	48.0	0.003
	Styrene	12.0	
	Sec.-Butyltitanate	40.0	
VII.	Polyester	48.75	0.030
	Methyl methacrylate	16.25	
	Sec.-Butyl titanate	35.00	
VIII.	Polyester	45.0	0.003
	Methyl methacrylate	15.0	
	Styrene	10.0	
	Sec.-Butyl titanate	30.0	
IX.	Polyester	48.0	0.003
	Styrene	32.0	
	Isopropyl titanate	20.0	
X.	Polyester	43.27	0.003
	Styrene	14.42	
	Sec.-Butyl titanate	28.84	
	Raw tung oil	13.46	
XI.	Ethylene glycol maleate polyester (40% styrene modified).	54.0	
	Styrene	36.0	.003
	Sec.-Butyl titanate	10.0	

I claim:

1. A stable quick-drying vehicle for coating materials comprising an unsaturated polyester, a vinyl-type monomer capable of undergoing addition polymerization with the unsaturated polyester, and a titanium orthoester, said polyester vinyl monomer and titanium orthoester being adapted to quick drying when exposed in a thin film to cold energy.

2. A vehicle according to claim 1, in which the monomer is present in an amount approximately 10% to 70% by weight of the polyester.

3. A vehicle according to claim 1, in which the titanium orthoester is present in an amount approximately 20% to 150% by weight of the polyester.

4. A vehicle according to claim 1, in which the monomer is styrene.

5. A vehicle according to claim 1, in which the titanium orthoester is sec.-butyltitanate.

6. A stable quick-drying vehicle for coating materials, comprising an unsaturated polyester, a vinyl-type monomer capable of undergoing addition polymerization with the unsaturated polyester, a drying oil and a titanium orthoester, said vehicle being adapted to quick drying when exposed in a thin film to cold energy.

7. A vehicle according to claim 6, in which the drying oil is present in an amount which is approximately 30% by weight of the polyester.

8. A stable quick-drying printing ink, comprising an unsaturated polyester, a vinyl-type monomer capable of undergoing addition polymerization with the unsaturated polyester, a titanium orthoester and a pigment, said ink being adapted to quick drying when exposed in a thin film to cold energy.

9. A method for rapidly indurating a vehicle comprising an unsaturated polyester, a vinyl-type monomer capable of undergoing addition polymerization with the unsaturated polyester and a titanium orthoester, which comprises forming a solution of the polyester, monomer and titanate, forming a film of said solution, and irradiating said film with cold energy.

10. The method according to claim 9, in which said cold energy is ultra-violet light.

11. The method according to claim 9, in which said cold energy is the full spectrum of ultra-violet light.

12. In the art of printing a sheet, the improvement which comprises forming a solution of an unsaturated polyester, a vinyl-type monomer capable of undergoing addition polymerization with the unsaturated polyester, and a titanium orthoester, said solution having suspended therein a pigment to form an ink, printing the sheet with said ink, and irradiating the printed surface of the sheet with cold energy.

13. The improvement according to claim 12, in which said cold energy is ultra-violet light.

14. The improvement according to claim 12, in which said cold energy is the full spectrum of ultra-violet light.

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