

SPECIFICATION

Control of recoating time for water dilutable alkyd surface coating compositions

- 5 This invention relates to water dilutable alkyd surface coating compositions and to a method for adjusting the duration of the initial interval when such a composition can be recoated without wrinkling. 5
- Most water dilutable modified or unmodified alkyds are supplied as solutions of alkyd polymers in a strong polar solvent such as propasol (propoxy propanol), butyl cellosolve (ethylene glycol monobutyl ether) or a mixture of polar solvents. The alkyds are generally supplied at 60 to 75% concentration.
- 10 Relative to conventional hydrocarbon solvent soluble alkyds which have acid numbers of near zero to about ten, the water dilutable alkyds have acid numbers above about twenty, generally between 30 and 60. Because of their higher acidity they can be further reacted with amines or ammonia to give them water dilutability. 10
- Air drying clear varnishes can be made from these water dilutable alkyds by adding suitable drying agents, such as cobalt, zirconium and manganese naphthenates. 15
- However, at 60 to 75% solids concentration, these varnishes are too viscous to apply by conventional means such as brushing or roller coating. In order to reduce their viscosity they can be diluted by further addition of polar solvents, an ammoniacal aqueous solution, or a mixture of the two. Suitable brushing viscosities are thus obtained at concentrations of 25 to 40% on a weight to volume basis.
- 20 In many applications it is desirable to use more than one coat of the varnish. This gives added dry film thickness and better protection, while at the same time enhancing the appearance of the varnished surface. When more than one coat has to be applied it is necessary to apply the second coat at a suitable time after the first coat has been applied; otherwise the application of the second coat results in wrinkling. As an example, a particular varnish may be recoated within 5 to 10 hours of the application of the first coat. If the 25 second coat is applied between 10 and 28 hours of the application of the first coat, wrinkling may occur. However, after 28 hours the second coat may be applied anytime without causing any wrinkling. Thus, in this particular case there are two key time intervals suitable for recoating, the first between 5 hours and 10 hours, which will be referred to herein as "interval A", and the other anytime after 28 hours of the application of the first coat.
- 30 From a practical view point including convenience to the user of the varnish, it is important to be able to control the time periods during which the second coat may be applied without wrinkling. In particular, it is important to be able to extend the first period, interval A. 30
- In the above cited example the time interval, interval A, in which the second coat may be applied is given as 5 to 10 hours. Moreover, in this case the second coat may be applied anytime after 28 hours. These times 35 vary from alkyd to alkyd, depending upon the nature of the alkyd and the solvent system used. 35
- It has been found that by changing the content and type of drying agent, the time interval A may be changed. Thus, if the amount of drying agent added is reduced the time interval A may be extended. On doing so, however, the varnish dries more slowly, that is, remains tacky and soft for a long period. This is undesirable. When the varnish dries too slowly, it is apt to attract dust, thus marring its appearance.
- 40 Moreover, a varnished surface cannot be put to use unless the varnish has achieved a certain degree of hardness. 40
- Efforts to achieve the same affect without changing the drying time by adding a higher boiling solvent, such as butyl carbitol (boiling point 230.6°C) as compared to butyl cellosolve (boiling point 171.2°C) or propasol (boiling point 149.8°C) have produced little or no change in the interval A.
- 45 Varnishes based upon conventional hydrocarbon soluble alkyds are also prone to wrinkle when thick coats are applied. It was reasoned that by reducing the solids of the varnish based upon water dilutable alkyds, the film thickness deposited per coat may be reduced somewhat and this may enable control of the interval A. This approach, obviously, would be useful only if the dry film thickness achieved with two coats of lower solids varnish was still considerably more than the dry film thickness of one coat when a higher 50 concentration varnish was used. 50
- These attempts led to some surprising and unexpected results. It was found that diluting the varnish with the polar organic solvent alone or with a combination of polar organic solvent and water did not result in any significant change in the interval A. Actually, when the varnish was diluted below a certain critical solids concentration, its flow properties were drastically affected. Varnishes with solids concentration below this 55 critical concentration would not wet out on the first coat and would form "puddles" or discontinuities in the coating. 55
- It has now been discovered that the interval A, or the initial interval when such surface coating compositions can be recoated without wrinkling, can be changed by changing the weight ratio of the water to the organic polar solvent present in the solvent system for the water dilutable alkyd resin within certain 60 limits. The solvent system may be formed with one organic solvent or a mixture of organic solvents. It has been found that increases in the weight ratio of water to organic solvent provide increases in the duration of the initial wrinkle-free recoating interval, and decreases in the weight ratio provide decreases in the initial wrinkle-free recoating interval. 60
- Therefore according to one aspect of the present invention there is provided a protective coating 65 composition having a convenient recoating time comprising a water dilutable alkyl resin, drier for said resin, 65

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at least one organic polar solvent for said resin, and water, the weight ratio of water to organic solvent being at least 4.0:1.0, but less than the ratio which causes resin precipitation out of solution or discontinuities in the coating.

According to a further aspect of the invention there is provided a method for adjusting the duration of the initial interval when a protective coating composition can be recoated without wrinkling, said protective coating composition containing a water dilutable alkyl resin and a drier in a water-organic polar solvent system, the method comprising adjusting the weight ratio of water to organic polar solvent in the solvent system to at least 4.0:1.0 but less than the ratio which causes resin precipitation out of solution or discontinuities in the coating, to achieve the desired initial interval, increases in the weight ratio providing increases in the duration of said interval and decreases in the weight ratio providing decreases therein.

It has been found that when a varnish is formulated with a weight ratio of water to organic solvent of at least 2.9:1.0 the initial recoating interval is increased over prior art formulations. Generally, the weight ratio of water to organic solvent will be higher than 3.0:1.0 or 4.0:1.0 and preferably will be higher than 5.0:1.0.

These findings which provide increased initial recoating intervals are compared with the closest known prior art which is a water dilutable alkyd varnish that has been prepared by Cargill, Inc. These known formulations were prepared from a concentrate having 75% solids content. A formulation having 30% solids was obtained by diluting the concentrate with a weight ratio of water to organic solvent of 80/20. In contrast, the present compositions may start with similar concentrates of water diluted alkyd resins, but accomplish the dilution with water alone and thereby provide formulations containing a higher proportion of water in the solvent system.

In accordance with the present invention it has further been discovered that the maximum time duration for the initial interval for recoating without wrinkling is obtained when the weight ratio of water to organic solvent is substantially at the limit beyond which further increments in the water concentration would result in resin precipitation out of solution or discontinuities (puddling) in the coating. In one preferred embodiment in which the polar organic solvent is butyl cellosolve it has been found that the point at which discontinuities occur is when the weight ratio of water to organic solvent is 6:1. Therefore, the maximum length of the initial interval for recoating is obtained with a weight ratio of water to organic solvent which is slightly less than 6:1.

It should be noted that the particular water to solvent ratio limit where precipitation out of solution or discontinuities in the coating occur, will differ for different solvent systems and alkyd resins. Nonetheless, each system selected will provide the maximum initial recoating interval where the water to solvent ratio approaches such a critical limit.

The length of the initial recoating interval is also dependent upon the ambient temperature and humidity, with increased humidity increasing the initial recoating interval period. In all of the experimental work reported in this application the temperature was $70 \pm 5^\circ\text{F}$ and $45 \pm 5\%$ relative humidity.

The present compositions contemplate formulations containing any desired solids content. For most applications, particularly where it is desired to brush or roller coat the composition, the solids content of the composition will be in the range 25 to 40% on a weight to volume basis.

Apart from the adjustment of water in the water-organic solvent system, all other components of the present surface coating compositions including alkyd resins and drying agents are conventional.

The invention will be illustrated by the following Examples. Examples I, II and III describe varnish formulations which are used in the experiments described in Examples IV, V and VI.

Example I

This Example illustrates a typical procedure for making a varnish from a water dilutable alkyd. The drying agents used are in normal amounts for products of this type.

5		Parts by weight	5
	# 7407 water dilutable alkyd in Proposal P. (supplied by Cargill, Inc.) at 80% solids	340	
10	Ammonium hydroxide (28%)	26	10
	Butyl cellosolve	30	
	Deionized water	482	
15	The above components were mixed thoroughly, and then		15
	Tinuvin P paste (U.V. absorber)	7	
20	was added and the resulting mixture mixed until the solution was free of undissolved particles. Thereafter		20
	Cobalt naphthenate 6% (drier)	5	
	Zirconium Drier 12%	3	
25	Activ-8 (drier)	3	25
	Super Ad-it (bactericide)	1	
30	BYK 301 (wetting agent)	2.8	30
	Butyl cellosolve	10	
		909.8	
35			35
	were added.		
	The above varnish has a solids concentration of 30%		
40	Interval A: 5 to 15 hours		40
	Wrinkling Time: 16 to 28 hours		
	Water to solvent weight ratio : 4.2:1		

Example II

This Example also illustrates a typical procedure for making a varnish from a water dilutable alkyd. The drying agents used are half the normal amount for products of this type.

5		Parts by weight	5
	#7407 water dilutable alkyd in Proposal (supplied by Cargill, Inc.) at 80% solids	340	
10	Ammonium hydroxide (28%)	26	10
	Butyl cellosolve	30	
	Deionized water	482	
15	The above components were thoroughly mixed, and then		15
	Tinuvin P paste (U.V. absorber)	7	
20	was added and the resulting mixture mixed until the solution was free of undissolved particles. Thereafter		20
	Cobalt naphthenate 6%	2.5	
	Activ-8 (drier)	1.5	
25	Zirconium naphthenate 12%	1.5	25
	Super Ad-it (bactericide)	1	
30	BYK 301 (wetting agent)	2.8	30
	Butyl cellosolve	10	
		<u>904.3</u>	
35	were added.		35
	The above varnish had a solids concentration of 30%		
	Interval A: 5 to 24 hours		
	Wrinkling time: 25 to 35 hours		
40	Water to solvent weight ratio: 4.2:1		40

Example II

This Example illustrates a typical procedure for making a varnish from a water dilutable urethane modified alkyd. Normal amounts of drying agents, as per Example I, were used.

The following components were sequentially added and mixed thoroughly:

5		wt/gms	5
	Urethane modified waer dilutable alkyd, 70 in butyl cellosolve (XP4366, Spencer-Kellog)	354	
10	Ammonium hydroxide (28%)	15	10
	Deionized water	424	
15	Thereafter the following components were added and mixed:		15
	Butyl cellosolve	30	
	Cobalt hydrocure (drier) (Mooney)	1	
20	Manganese hydrocure (drier) (Mooney)	1	20
	Activ-8 (drier)	0.45	
25	L-5310 (20% in butyl cellosolve) (wetting agent)	2.5	25
	pH adjusted to 8.5		
		826.95	

30	The above varnish had a solids concentration of 30%	30
	Interval A: 5 to 17 hours	
	Wrinkling time: 18 to 32 hours	
	Weight ratio of water to cellosolve: 2.8:1.	

35	<i>Example IV</i>	35
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This Examples compares the varnishes of Examples I and II, showing the effect of changing the amount of drying agent on "wrinkle time" on recoating and on the drying time of the varnishes.

40	Two 2ft x 3ft. plywood panels were coated with a conventional clear sealer, allowed to dry for four hours and then lightly sanded.	40
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	The panels were then coated with varnishes of Example I and Example II. Three hours later, when the panels were dry to touch, they were divided into 40 squares each, each square clearly marked and separated by using a masking tape. To these squares was applied a second coat, different squares receiving a second coat at one hour intervals, starting with ten hours elapsed time after the initial coat was applied. Varnish of Example I and varnish of Example II were thus compared on these two separate panels. The time at which the application of the second coat resulting in wrinkling was noted. The time was measured from the time the first coat was applied.	45
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The results are reported below:

50		Drying Agents Used	Wrinkle Time on recoat (hrs.)	Touch Dry Time (hrs.)	Thorough Dry Time* (hrs.)	50
55	Varnish I (see Example I)	Normal Amount	16	2	16	55
	Varnish II (see Example II)	Half of Normal Amount	25	4	24+	

60	* Dry Times were determined using a Gardner Circular Dry Time Recorder.	60
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From the above it will be seen that reduction in drying agent level increased interval A but undesirably increased drying time.

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Example V

This Example shows the effect of the type of diluent used and its concentration of the "wrinkle time" on recoating.

The "wrinkle time" on recoating for each varnish was determined on separate panels as in Example IV.

- 5 The results are given in the following Table. The formulation employed had the composition of Example I with reduction in solids content being accomplished with addition of the listed diluents. 5

	Diluent added	% of N.V.	Wrinkle Time on Second Coat (hrs.)	
10	a) None	30	12	10
	b) $\frac{20}{80} = \frac{\text{butyl cellosolve}}{\text{water}}$	28	12	
15	c) Water alone	28	18	15
		27	24	
		26	32	
		25	48	
		24	60+	
20		23	wetting problem	20

Example VI

This Example was carried out in the same manner as Example V except that the formulation employed had the composition of Example III. The results are as follows:

	Diluent Added	Concentration (wt. %)	Wrinkle Time on Second Coat (hrs.)	
25	a) None	30	16	25
	b) Butyl carbitol	28	16	
30	c) Butyl cellosolve	28	16	30
		23	wetting problem	
	d) $\frac{20}{80} = \frac{\text{butyl cellosolve}}{\text{water}}$	28	18	
35		24	20	35
	4) Water alone	28	24+	
		27	36+	
		26	40+	
		25	60+	
40		24	wetting problem	40

From the above Examples V and VI it will be seen that increasing water concentration increased the "wrinkle time" on recoating until the critical limit was reached.

- 45 It is also to be noted from Examples V and VI that some formulations may have succeeded in lengthening the "wrinkle time" to such an extent (more than 60 hours) that these formulations may no longer have a "wrinkle time" and may be recoatable at any time after becoming touch dry. In these cases interval A or the initial interval for recoating without wrinkling may be infinite. 45

The word "Cellosolve" is a registered Trade Mark.

50 CLAIMS 50

1. A protective coating composition having a convenient recoating time comprising a water dilutable alkyl resin, drier for said resin, at least one organic polar solvent for said resin, and water, the weight ratio of water to organic solvent being at least 4.0:1.0, but less than the ratio which causes resin precipitation out of solution or discontinuities in the coating. 55
2. A composition as claimed in Claim 1, in which the weight ratio of water to organic solvent is substantially at the limit beyond which the resin precipitation out of solution or discontinuities in the coating occur whereby substantially a maximum duration of the initial recoating interval is obtained.
3. A composition as claimed in Claim 1 or Claim 2, in which the solids content of the composition is from 25 to 40% on a weight to volume basis. 60
4. A composition as claimed in any preceding claim, in which the alkyd resin is urethane modified.
5. A composition as claimed in any preceding claim, in which the organic solvent is diethylene glycol monobutyl ether, ethylene glycol monobutyl ether or propoxy propanol.
6. A composition as claimed in Claim 5, in which the organic solvent is ethylene glycol monobutyl ether. 65



Example V

This Example shows the effect of the type of diluent used and its concentration of the "wrinkle time" on recoating.

The "wrinkle time" on recoating for each varnish was determined on separate panels as in Example IV.

- 5 The results are given in the following Table. The formulation employed had the composition of Example I with reduction in solids content being accomplished with addition of the listed diluents. 5

Diluent added	% of N.V.	Wrinkle Time on Second Coat (hrs.)	
10 a) None	30	12	10
b) $\frac{20}{80} = \frac{\text{butyl cellosolve}}{\text{water}}$	28	12	
15 c) Water alone	28	18	15
	27	24	
	26	32	
	25	48	
	24	60+	
20	23	wetting problem	20

Example VI

This Example was carried out in the same manner as Example V except that the formulation employed had the composition of Example III. The results are as follows:

Diluent Added	Concentration (wt. %)	Wrinkle Time on Second Coat (hrs.)	
25 a) None	30	16	25
30 b) Butyl carbitol	28	16	30
c) Butyl cellosolve	28	16	
	23	wetting problem	
d) $\frac{20}{80} = \frac{\text{butyl cellosolve}}{\text{water}}$	28	18	
35	24	20	35
4) Water alone	28	24+	
	27	36+	
	26	40+	
40	25	60+	40
	24	wetting problem	

From the above Examples V and VI it will be seen that increasing water concentration increased the "wrinkle time" on recoating until the critical limit was reached.

- 45 It is also to be noted from Examples V and VI that some formulations may have succeeded in lengthening the "wrinkle time" to such an extent (more than 60 hours) that these formulations may no longer have a "wrinkle time" and may be recoatable at any time after becoming touch dry. In these cases interval A or the initial interval for recoating without wrinkling may be infinite. 45

The word "Cellosolve" is a registered Trade Mark.

CLAIMS 50

1. A protective coating composition having a convenient recoating time comprising a water dilutable alkyl resin, drier for said resin, at least one organic polar solvent for said resin, and water, the weight ratio of 55 water to organic solvent being at least 4.0:1.0, but less than the ratio which causes resin precipitation out of solution or discontinuities in the coating. 55
2. A composition as claimed in Claim 1, in which the weight ratio of water to organic solvent is substantially at the limit beyond which the resin precipitation out of solution or discontinuities in the coating occur whereby substantially a maximum duration of the initial recoating interval is obtained.
3. A composition as claimed in Claim 1 or Claim 2, in which the solids content of the composition is from 60 25 to 40% on a weight to volume basis. 60
4. A composition as claimed in any preceding claim, in which the alkyd resin is urethane modified.
5. A composition as claimed in any preceding claim, in which the organic solvent is diethylene glycol monobutyl ether, ethylene glycol monobutyl ether or propoxy propanol.
6. A composition as claimed in Claim 5, in which the organic solvent is ethylene glycol monobutyl ether. 65



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7. A composition as claimed in any preceding claim, in which the weight ratio of water to organic solvent is slightly less than 6:1.
8. A composition as claimed in any preceding claim, in which the weight ratio of water to organic solvent is at least 5.0:1.0.
- 5 9. A protective coating composition substantially as herein described with reference to any one of the Examples. 5
- 10 10. A method for adjusting the duration of the initial interval when a protective coating composition can be recoated without wrinkling, said protective coating composition containing a water dilutable alkyd resin and a drier in a water-organic polar solvent system, the method comprising adjusting the weight ratio of water to organic polar solvent in the solvent system to at least 4.0:1.0 but less than the ratio which causes resin precipitation out of solution or discontinuities in the coating to achieve the desired initial interval, increases in the weight ratio providing increases in the duration of said interval and decreases in the weight ratio providing decreases therein. 10
- 15 11. A method as claimed in Claim 10, in which the weight ratio of water to organic polar solvent is increased to increase the duration of said interval. 15
12. A method for adjusting the duration of the initial interval when a protective coating composition can be recoated without wrinkling substantially as herein described with reference to any one of the Examples