Coating Properties of Alkyd–Ketonic (cyclohexanone formaldehyde) Resin Blends

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ABSTRACT: The present article describes the preparation and coating properties of long oil-length alkyd and ketonic (cyclohexanone formaldehyde) resin blends. A unique solvent system, which shows a one-phase clear solution and a clear coat of the binder system, was used. The scope of the article is to produce a better combination of properties than those of the individual components. It has been observed that, when a 30% concentration of ketonic resin was blended with the alkyd resin, a significant improvement in adhesion, hardness, gloss, storage stability, acid resistance, and drying time was achieved over that of the alkyd resin alone.
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KEY WORDS: Alkyd resin, blends, coating properties, cyclohexanone formaldehyde (ketonic) resin.

Polymer blends have become important for both scientific investigation and commercial product development, because polymer blends can be tailored to meet the requirements of specific applications. They can be developed much more quickly than new polymers and require less capital investment.

Several patents are available where ketonic (cyclohexanone formaldehyde) resin is used as an additive to improve the coating properties of alkyd resins (1–4). However, no detailed study has been reported on the blending of two resins. Therefore, it was necessary to undertake a comprehensive study of the effect of blended resins on the coating properties.

Essentially, the present paper reports the effect of blended resins (alkyd and ketonic) on the coating properties, such as hardness, adhesion, flexibility, gloss, chemical resistance, storage stability, and drying time.

MATERIALS AND METHODS

Refined linseed oil was obtained from Mahendra Oil Mill (Mumbai, India). Pentaerythritol was purchased from Manali Chemicals (Mumbai, India). Phthalic anhydride (minimal assay 99.5%) for the reaction was procured from S.D.Finechem Ltd. (Mumbai, India). Litharge (minimal assay 98%) from Loba chemie (Mumbai, India) was used as a catalyst.

A 65% oil-length linseed penta-alkyd was prepared in the laboratory by using the following formulation (5) (calculation was based on 100% resin yield; all measurements are expressed in weight percentage):

Linseed oil, refined	65.00
Pentaerythritol	12.78
Phthalic anhydride	25.29
Catalyst (litharge)	0.01
	103.08
Water of reaction	–3.08
Resin yield	100.00

Ketonic resin (see Table 1 for specifications) was procured from M/s Hindustan Inks (Mumbai, India).

Solvent system. Fundamental factors that affect the properties of blends include (i) equilibrium phase and interfacial behavior, (ii) physical and chemical interactions between the component's phase morphology, and (iii) rheology, all of which relate to pragmatic issues of compatibility.

Alkyd resin has good compatibility with ketonic resin in industrial solvents that are most frequently used. However, to achieve desired results of solvency, evaporation rate, and phase separation, several combinations of solvents were tried. The solvent system that produced a one-phase clear solution and a clear coat of the binder system was as follows: toluene, 60 wt%; cyclohexanone, 20 wt%; butanol, 20 wt%.

All solvents were of analytical grade and were used without further purification. These solvents of minimal assay 99% (gas chromatography) were purchased from S.D.Fine chem Ltd.

The alkyd and ketonic resins were individually thinned to 50% solids with the above solvent system. The thinned resins were then blended in different proportions.

Driers. Driers used in the present study were purchased from Narchem Industries (Mumbai, India) and were used for the blends as follows: zirconium octoates (6%), 0.2; lead naphthanate (18%), 0.3; and manganese octoates (6%), 0.1. The percentages of driers are based on the resin solids.

Coating properties testing. Drying time (6): The samples were applied onto mild steel panels. The time was then noted for surface drying and tack-free drying with and without addition of driers.

Hardness (7): The uniformly coated panels were allowed to dry for 1 wk before testing. A relative measurement of hardness was achieved by rating the hardness of lead pencils.

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TABLE 1

Sales specification	Value-unit	Test method
Melting point	92–108°C	DIN 4625
Gardner color 50% in butyl acetate/*n*-butanol (85:15)	<2	ASTM D 1544-80
Density at 20°C	1.13–1.14 g/cm^3	DIN 53 479-B
Acid number	0.3 mg KOH/g	DIN 53 402
Hydroxyl number	*ca.* 330 mg KOH/g	DIN 53 240, ASTM E 222-67
Water content	4 Max. by wt	DIN 51 777.part1

Gloss (8): Gloss of a film is the measurement of how well a surface functions as a mirror. Gloss characteristics of coated glass panel films were measured with a sheen gloss meter at an angle of 60°.

Adhesion (7): Coated panels were allowed to mature for a week before undergoing the test. The cross-cut adhesion method was employed to perform the adhesion test.

Flexibility (9): This property is related to elongation and it can be measured by the conical mandrel test. The samples were coated on tin plates for checking flexibility with a 1/4" conical mandrel.

Storage stability: Storage stability of the samples was studied by storing them in cylindrical sample containers for 4 mon, after which the condition of the surface was visually observed.

Chemical resistance (10): For the water immersion test, glass panels were coated with the samples and allowed to dry for 3 d. The ends of the glass panels were coated with wax to prevent water migration under the film from the open ends. The panels were then dipped into water and examined for changes in appearance after 24 h. For the acid immersion test, coated glass panels were prepared, similar to those for the water immersion test. These panels were dipped into 3% (w/w) sulfuric acid solution, and changes in appearance were monitored after 24 h.

RESULTS AND DISCUSSION

A detailed study was carried out on the coating properties of different blend ratios. The blends that contained ketonic resin at less than 10% (w/w) concentration showed no significant changes.

When the concentration of ketonic resin was increased to 50% and up, surface drying became possible without the addition of driers, as shown in Table 2. However, tack-free time could not be achieved for any of the ratios.

When tested with driers, surface drying and tack-free drying times were improved when the concentration of ketonic resin was increased in the blends. This may be because of the presence of carbonyl groups, which activate the methylene groups in the ketonic resin. Therefore, in the presence of suitable driers, the oxygen activation of the methylene group is further accelerated, which results in faster drying.

Hardness. Pencils graded from 5B to 5H were tested on coated mild steel panels. Table 3 shows that hardness increases initially for alkyd-ketonic resin blends up to 80:20 (w/w) concentration; then it levels off up to 60:40 ratio and further decreases gradually up to 100% ketonic resin concentration. Therefore, the optimal concentration of ketonic resin, blended with alkyd resin to achieve better hardness, seems ideally to be between 20 and 40%.

Gloss. Generally, long oil-length alkyds are semiglossy. Ketonic resin is known for its light color, good gloss, and excellent light stability. Table 3 shows a gradual increase in gloss of the blend with increasing concentration of ketonic resin.

Adhesion and flexibility. Long oil-alkyd resins have usually moderate adhesion. However, the adhesion of alkyd resin can be improved by the incorporation of ketonic resin. The results in Table 4 show the enhancement of adhesion in the blends when the concentration of ketonic resin is increased. All samples tested for flexibility passed the 1/4″ bend test,

TABLE 2
Drying Time

	Surface drying		Tack-free drying	
Alkyd/ketonic composition (% w/w)	Without driers (min)	With driers (min)	Without driers (min)	With driers (min)
100:0	—	50	—	220
90:10	—	50	—	215
80:20	—	45	—	195
70:30	—	40	—	190
60:40	—	40	—	180
50:50	45	35	—	175
40:60	40	30	—	170
30:70	35	30	—	160
20:80	30	25	—	160
10:90	30	25	—	155
0:100	25	25	—	150

TABLE 3
Gloss and Pencil Hardness

Alkyd/ketonic (% w/w)	Gloss (at 60°)	Hardness (lead pencil)
100:0	78	2H
90:10	80	4H
80:20	81	5H
70:30	83	5H
60:40	83	5H
50:50	84	4H
40:60	85	2H
30:70	89	2H
20:80	89	H
10:90	90	H
0:100	92	HB

TABLE 4
Adhesion and Flexibility

Alkyd/ketonic (% w/w)	Adhesion (%)	Flexibility
100:0	72	Pass
90:10	85	Pass
80:20	96	Pass
70:30	100	Pass
60:40	100	Pass
50:50	100	Pass
40:60	100	Pass
30:70	100	Pass
20:80	100	Pass
10:90	100	Pass
0:100	100	Pass

TABLE 5
Storage Stability

Alkyd/ketonic (% w/w)	Skinning tendency (after 4 mon)
100:0	Heavy skinning
90:10	Skinning
80:20	Slight skinning
70:30	No skinning
60:40	No skinning
50:50	No skinning
40:60	No skinning
30:70	No skinning
20:80	No skinning
10:90	No skinning
0:100	No skinning

and more surprisingly, not only a simple manual bend over/bend back test, but even when the coated tin panels were rolled over the conical mandrel through any angle no cracks were observed.

Storage stability. Even after storing the samples for 4 mon, no distinctive layers were observed. This shows good compatibility of the two resins.

When the alkyd resin was stored without the addition of driers, it showed no skinning tendency. However Table 5 shows that the alkyd resin was prone to heavy skinning up to an alkyd/ketonic ratio of 80:20, which must be due to the effect of driers. Nevertheless, when the ketonic resin concentration was increased above 20%, the resulting blends were skin-free. This observation strongly suggests that ketonic resin can be used as an additive for improving the storage stability of alkyd resin.

Chemical resistance. Glass panels, coated with alkyd resin or its blend with 10% ketonic resin showed a slight blush when immersed in 3% sulfuric acid. However, when the concentration of ketonic resin in the blend was above 20%, the coated films remained unaffected, as shown in Table 6.

Table 6 clearly shows that up to 20% ketonic resin concentration the blend showed a slight blush, but with the increase

TABLE 6
Chemical Resistance

Alkyd/ketonic (% w/w)	Acid (3% H_2SO_4) immersion test appearance after 24 h	Water immersion test appearance after 24 h
100:0	Slight blush	Slight blush
90:10	Slight blush	Slight blush
80:20	Unaffected	Slight blush
70:30	Unaffected	Blush
60:40	Unaffected	Blush
50:50	Unaffected	Blush
40:60	Unaffected	Heavy blush
30:70	Unaffected	Heavy blush
20:80	Unaffected	Heavy blush
10:90	Unaffected	Heavy blush
0:100	Unaffected	Heavy blush

in the concentration of ketonic resin in the blend from 30% upwards, poor water resistance was observed.

From the preceding study one can conclude that, when an optimal [30% (w/w)] concentration of cyclohexanone formaldehyde resin is blended with alkyd resin, significant improvements in adhesion, hardness, gloss, storage stability, acid resistance, and drying time are achieved. These enhancements in the properties of the alkyd resin can be attributed to the excellent compatibility of ketonic resin with alkyd resin.

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