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The effects of alkyd/melamine resin ratio and curing temperature on the properties of the coatings

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Abstract: Synthetic resins are used as binders in protective coatings. An alkyd/melamine resin mixture is the usual composition for the preparation of a coating called "baking enamel" cured through functional groups of resins. The effects of the alkyd/butylated melamine resin ratio (from 85/15 to 70/30) and curing temperature (from 100 °C to 160 °C) on the crosslinking and properties of the coating are presented in this paper. The degree of curing was determined by differential scanning calorimetry. These data were used for the estimation of the degree of crosslinking. The hardness, elasticity, impact resistance, degree of adherence and gloss were also determined. Optimal coating properties could be achieved with an alkyd/melamine resin ratio of 75/25, a curing temperature of 130 °C and a curing time of 30 min.

Keywords: melamine modified alkyd resin, curing, coating properties.

INTRODUCTION

The objectives of organic coating technology are relatively thin polymer-matrix films adhered to solid substrates to perform decorative, protective or special functions. Organic coatings are formed by spreading and subsequent hardening of fluid coating compositions. In terms of their formulation, a coating composition, in general, includes a polymer binder (or a combination of binder components), pigments and extender (or fillers), carrier components (volatile liquids in liquid paints, air in powder coatings), and of course a number of functional additives. Depending on their field of application, coantings must possess various but well specified combinations of optical, mechanical (including adhesion durability), diffusion and sometimes also special properties (electrochemical, heat stability, dielectric properties).[1]

Alkyd resins are the most popular and useful synthetic resins applied as the binder in protective coatings. Frequently they are not used alone but are modified

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in the manufacture of the coatings. Modification of alkyd resins is usually carried out by other synthetic resins (melamine, acrylic, silicone). The resin blend technique is a simple and useful method for improving the properties of paints and varnish paints. The concept of a resin blend is based on the blending of resins in order to improve their advantages or on the blending of minor resin components to compensate the deficiencies of the main resin.[2]

Melamine resins are extensively used in coating systems. The amino resin is a minor constituent and plays the role of a crosslinking agent to join molecules of the other resin into a crosslinked network.[3] To achieve solubility in organic systems, the melamine resin is combined with an alcohol, such as *n*-butanol or methanol.

Literature data about the investigation of alkyd/melamine resin blends as the binder in protective coatings are rarely published. Attention was more often dedicated to other resin blends. A study of Ho and Ma[4] reviews polymeric coating of silicone modified alkyd resins while Carr and Wallston investigated alkyd/acrylic resin combinations.[5] It has been observed that, when a 30 % concentration of a ketonic resin was blended with an 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.[6] Melamine resin as the crosslinker in a combination of a dialkyl malonate blocked polyisocyanate and an acrylic polyol gives coatings with good chemical resistance properties.[7] A new four-step synthetic route for combining chromophores with melamine resins was developed and their use for optical applications was demonstrated.[8] The paper of Kalenda and Kalendova[9] discusses the influence of the variation of the melamine and alkyd resin components on the properties of the obtained films. The formaldehyde emitted during the curing of such resin systems and the methods available for the control of such emissions were also considered. The resistance of the cured films of various resin blends to a range of aggressive agents was also presented.[9]

The properties of coatings are strongly dependent on film formation.[10] If an alkyd resin is synthesized on the basis of undry oils (or saturated fatty acids) it is unable to form the coating film by itself but only in combination with other resins. The curing of alkyd resin by a melamine one is effected over their functional groups:

$$-N-\overset{|}{CH}-O-C_4H_9 \;+\; HO-R \;\rightarrow\; -N-\overset{|}{CH}-O-R \;+\; C_4H_9OH$$

part of butylated melamine resin — alkyd resin

The presented reaction is very complex, involving simultaneously a number of other secondary reactions.[11] Although alkyd/melamine resin blends have been used for many years for the manufacture of coatings, the relation between the curing reactions and the coating properties has not been sufficiently investigated.

An alkyd/melamine resin blend is the usual composition for the preparation of coatings called "baking enamel". The mixture is cured at elevated temperatures (from 80 °C to 200 °C for a time of 20 to 30 min). The results of the effects of the alkyd/butylated melamine resin weight ratio (from 85/15 to 70/30) and the curing temperature (from 100 °C to 160 °C) on the crosslinking and properties of the coatings are presented in this paper.

EXPERIMENTAL

Mateials

A phthalic alkyd resin containing 25 wt. % of saturated fatty acids, produced by "Helios" (Domzale, Slovenia), was used as a 70 % solution in methoxypropyl acetate. The characteristics of the resin were: acid number = 15 mg KOH/g; viscosity at 23 °C = 5000 mPa s; density = 1.067 g/cm^3.

A butylated melamine resin, produced by "Helios" (Domzale, Slovenia), was used as a 56 % solution in isobutyl alcohol. The characteristics of the resin were: acid number = 2 mg KOH/g; viscosity at 23 °C = 500 mPa s; density at 23 °C = 1.010 g/cm^3.

A mixture of solvents: 70 vol. % of "Celosolve" acetate, 20 vol. % of butyl alcohol and 10 vol. % of butyl glycol acetate.

Methods

Preparation of coatings. Alkyd and melamine resins were mixed in a dissolver. Then the mixture of solvents was added to control the viscosity. An experimental metallic panel was smeared with a thin layer of the prepared "enamel". Curing of coating was carried at temperatures from 100 °C to 160 °C for 30 min. Then the panel with coated film was left for 24 h at room temperature. The thickness of the dry coating film was 30 μm. The designations and the compositions of the samples are presented in Table I.

TABLE I. Designations and the compositions of the prepared coatings

Number of sample	Alkyd/melamine resin ratio	Curing temperature/°C				
		100	120	130	140	160
1	85/15	1a	1b	1c	1d	1e
2	80/20	2a	2b	2c	2d	2e
3	75/25	3a	3b	3c	3d	3e
4	70/30	4a	4b	4c	4d	4e

Determination of the properties of the dry coating film. The hardness of the coating film was determined by the standard method JUS H. C8. 055 using a Koning's bell-clapper. The bell-clapper was placed on a panel with a coating film under an angle of 6 degrees and left to oscillate. The elapsed time (in s) until the measured amplitude of the oscillation had decreased to 3 degrees is defined as the hardness.

The drawing elasticity was determined by the standard method JUS C. T7. 371 using an Erichsen's instrument for "deeply drawing". A semi-sphere like cup hits a panel with coating film and performs "deeply drawing". The distance from the zero position of cup to the moment when the film cracks is defined as the drawing elasticity (in mm).

The twist elasticity was determined using a standard method DIN 53211 by twisting a panel with a coating film over a metallic stick of defined diameter. During the specified time the coated film should not crack and separate from the panel.

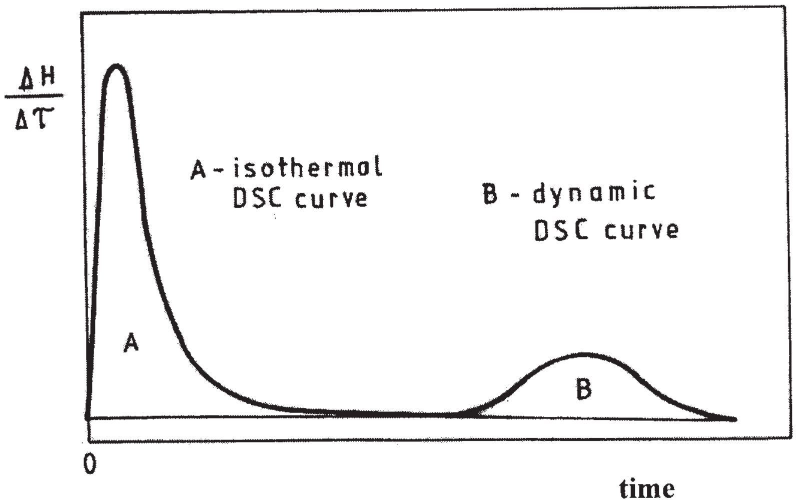

Fig. 1. Typical DSC thermogram of alkyd/melamine resin blend curing (Sample 1c; T = 130 °C; resin ratio 85/15).

The impact resistance was measured in accordance with the standard method JUS H. C8. 050 using an Erishsen's instrument, using a weight falling onto the coating film. The impact resistance is expressed in kg/cm^2.

The degree of film adherence to the base (panel) was measured by the standard method JUS H. C8. 059. The coated film was cut into small quadratic areas (1 × 1 mm). If none of them separate from the panel, the degree of film adherence is the best (that value is denoted as GT-0).

The gloss of the coating film was determined with "Byk Chemie" automatic instrument using an optical prism, under an angle of 60 degrees.

Determination the degree of curing. The degree of curing of the alkyd/melamine resin blend was determined by differential scanning calorimetry (DSC), using a Du Pont Model 910 instrument, under isothermal conditions in the temperature range 100–130 °C, and in the dynamic thermal range by further heating of the sample from the temperature of isothermal curing up to 200 °C. Small amounts of resins blend were encapsulated in standard Du Pont sample pans. The samples were then placed in the DSC, the temperature manually set to the desired value and the curing exotherms recorded on a chart recorder. After each isothermal curing, the uncured resins content was determined by heating the sample to 200 °C at a heating rate of 10 °C/min. A typical DSC thermogram of resin curing is given in Fig. 1. The heats evolved in the reaction (proportional to the amount of cured resins) were calculated from the areas between the DSC curve and the baseline, which were obtained by back-extrapolation of the horizontal straight line recorder after completion of the curing.[12] The total reaction enthalpy of the liquid reactive resin is proportional to the sum of areas A (under isothermal DSC curve; Fig. 1, A) and B (under dynamic DSC curve; Fig. 1, B). The analytical parameter in DSC is the so-called residual crosslinking enthalpy, *i.e.*, the heat liberated by the post-curing reaction of the sample from the temperature of isothermal curing up to 200 °C, proportional to the area under the dynamic DSC curve (Fig. 1, B). The areas A and B were calculated by numerical integration of the DSC thermograms using the Simpson method. The ratio of A to the total reaction enthalpy of the liquid reactive resin, (A+B), gives the degree of curing.[13]

DSC yields highly reproducible values for the degree of curing. It has the advantage of not being laborious and extremely small specimens (weighing *ca.* 20 mg) are used.

RESULTS AND DISCUSSION

The determined properties of the dry coating films are given in Table II. Samples 3a and 4a (cured at a temperature of 100 °C) are missing from Table II because they were sticky to touch and unsuitable for investigation.

As expected, the hardness of the coating films increases with increasing ratio of melamine resin in the blend and with curing temperature. The functionality of the melamine resin (containing three methylol groups) is higher than that of the alkyd resin which results in the formation of a more crosslinked coating film at higher ratios of melamine in the blend. The minimal acceptable value for the hardness is 40 s according to the standard method JUS H. C8. 055. The films formed at a curing temperature of 100 °C are sticky to touch and without acceptable value for hardness.

The minimal value for the drawing elasticity is 6 mm according to the standard JUS C. T7. 371. All the investigated coating films have satisfactory values (mostly between 9 and 10). The drawing elasticity decreases with increasing curing temperature but is independent of the resin ratio.

The values for the twist elasticity of the coating films are the same and very good for all the prepared samples (1/8 inch, 3 mm), and are independent of the resin ratio and curing temperature. The maximum value has to be 1/4 inch (6 mm).

The minimal acceptable value for the impact resistance of a coating film is 20 kg/cm^2. The determined values are very high (about 80 kg/cm^2).

The values for the film adherence (GT-0 for all samples) and gloss (95 to 99 %; minimal acceptable value is 80 %) are excellent.

TABLE II. Properties of coating films

Number of specimen	Hardness/s	Drawing elasticity mm	Impact resistance kg/cm^2	Gloss/%
1a	25	7.6	56	98
1b	49	10.4	82	95
1c	70	10.1	82	95
1d	94	9.9	82	99
1e	126	9.0	82	99
2a	25	–	56	98
2b	97	10.2	82	95
2c	120	10.0	82	99
2d	140	9.8	82	99
2e	150	9.0	82	99
3b	140	10.0	82	98
3c	150	9.9	82	99
3d	160	9.7	82	99

TABLE II. Continued

Number of specimen	Hardness/s	Drawing elasticity mm	Impact resistance kg/cm^2	Gloss/%
3e	168	8.8	82	93
4b	145	9.9	82	99
4c	160	9.6	82	99
4d	170	9.5	82	96
4e	180	8.7	78	95

On the basis of the obtained experimental results (Table II), and taking into consideration the economic factor, it can be seen that suitable coating properties could be achieved with an alkyd/melamine resin ratio of 75/25, a curing temperature of 130 °C and a curing time of 30 min. Curing temperatures above 130 °C are technologically unfavourable.

From the DSC curves of the curing of the alkyd/melamine resin blends, the degrees of curing were calculated using the method described in the experimental part. The values are given in Table III.

TABLE III. The effects of alkyd/melamine resin ratio and curing temperature on the degree of curing

Number of sample	Alkyd/melamine resin ratio	Degree of curing/%		
		100 °C	120 °C	130 °C
1	85/15	37	65	87
2	80/20	38	70	91
3	75/25	56	71	92
4	70/30	61	73	97

The degree of curing of the resins blend is an indicator of the content of reacted functional groups up to a definite time of reaction, at a certain temperature. These data can be used for the estimation of the degree of crosslinking. The degree of curing (Table III) increases with increasing ratio of melamine resin in the resin blend, and with increasing the curing temperature. A significant increase in the hardness of the coating film with increasing of both above-mentioned parameters was shown in this investigation, so the degree of curing has a pronounced effect on the hardness of the obtained film.

CONCLUSION

The effects of alkyd/melamine resin ratio and curing temperature on the crosslinking and properties of coatings were investigated. The degree of curing increases with increasing ratio of melamine resin in the resin blend, and with curing temperature. The hardness of a coating film increases with increasing degree of curing while the elasticity slightly decreases. Favourable coating properties could be achieved with an alkyd/melamine resin ratio of 75/25, a curing temperature of 130 °C, and a curing time of 30 min.

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И З В О Д

УТИЦАЈ ОДНОСА АЛКИДНА/МЕЛАМИНСКА СМОЛА И ТЕМПЕРАТУРЕ УМРЕЖАВАЊА НА СВОЈСТВА ПРЕМАЗА

РАДМИЛА Ж. РАДИЧЕВИЋ И ЈАРОСЛАВА К. БУДИНСКИ-СИМЕНДИЋ

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Основне компоненте у заштитним премазима су синтетске смоле. Смеша алкидна/меламинска смола се обично користи као везиво у тзв. "емајл/лаковима" који умрежавају на повишеним температурама преко функционалних група смола. У овом раду истраживан је утицај масеног односа алкидна/меламинска смола (од 85/15 до 70/30) и температуре умрежавања (од 100 до 160 °C) на степен умрежења и својства филма премаза: тврдоћу, еластичност, отпорност на удар, степен пријањања и сјај. Степен умрежења расте са порастом удела меламинске смоле у смеши, као и са температуром умрежавања. Тврдоћа филма премаза расте са порастом степена умрежења док еластичност незнатно опада. Најповољнија температура умрежавања је 130 °C у времену од 30 min (узимајући у обзир и економску оправданост), а однос алкидна/меламинска смола 75/25.

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