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The Significance of the Ratio of Alkyd-Amino Resins on Curing Temperature and Performances of Stoving Paints

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Abstract—**Alkyd resin, polyester, acrylic, epoxy, polyurethane, natural resins and some other synthetic resins are used as binders in the manufacturing of paints and protective coatings. A blend of alkyd and amino (butylated melamine formaldehyde, i.e. BMF) resins is a common composition for the formulation of the specific coating called "baking or stoving enamel" that is cured by baking or stoving at a certain temperature and time for crosslinking of functional groups of blended resins. In this research paper, the significance of the ratio (80:20, 75:25, 70:30 and 50:50) of alkyd-amino resins, curing temperature (from 100°C to 140°C) for crosslinking reactions, and the difference in performances of the coatings have been explored and described as well. The extent of curing has been determined by differential scanning calorimeter. Obtained data have been used for the assessment of the degree of crosslinking reactions between functional groups of alkyd and amino resins. The adhesion property, gloss, hardness, elasticity, impact resistance have also been evaluated. Best possible performance of coatings have been attained with a ratio (75:25) of alkyd-amino resins with a curing temperature of 130±2°C and curing time of 30 minutes.**

Index Terms—**Alkyd-amino resins, crosslinking agent, curing temperature, adhesion property, stoving paint.**

I. INTRODUCTION

Paints are the designed combinations of four fundamental constituents i.e., resin, pigment, solvents and additives, which when applied to the object's surfaces form solid, hard and protective films after curing. In the prehistoric time, paints were prepared from plants-extracts (i.e., natural gums and natural resins), egg-shells, insects, animal's fat, grinded rocks and minerals as pigment, and water as a common solvent. Paint preparations have been improved gradually by applying modern techniques and technology to get superior quality of surface coatings [1,2,3]. Methodical study has publicized that modern paints are being prepared to comprise shape (amorphous to crystalline), size (from micron to nano), configuration, dispersion steadiness, film-uniformity, better appearance, enforced quality and robustness to both exterior and interior finishes of automotive vehicles by incorporation of suitable constituents [2,3,7,9]. The surface coating technology has been more sophisticated in automobile sector for the requirements of various categories of the end-users. Optimum preparation was done to get proper blends of resins, compatible solvents, pigments, fillers, additives, curing agents and extenders for the purpose of better protection and to inhibit corrosion, cracks, erosion, resistance to heat, fire and cosmic rays, and has been designed to withstand in other adverse weathering and environmental conditions [1,2,10,16].

The purpose of paint coatings is to get relatively thin polymer-matrix film that should be adhered to solid substrate surfaces to perform decorative, protective and some specific functions. Surface coating films are formed by applying, spreading, subsequently curing and hardening of fluid coatings. In terms of the formulation, a coating composition generally includes a polymer binder (or a combination of the binders), pigment, functional additives, solvents, extender (or fillers) and the carrier components (i.e. volatile parts in liquid paints or air in powder coatings). Depending on their fields of applications, coatings must possess various but well specified combinations of optical, mechanical (including adhesion & durability), diffusion and sometimes also special properties i.e. electrochemical, heat resistance stability, dielectric properties etc [5,6,7].

Alkyds and polyesters are the most accepted and useful synthetic resins, applied as the binders in protective coatings. Normally they are not used alone but are modified for the manufacturing of different coatings as per requirements of industries. Modification of alkyd resins is usually carried out by other synthetic resins (melamine, acrylic or silicone). The resin blend technique is a simple and useful method for improving the properties of paints and varnishes. The concept of a resin blend is based on the blending of resins in order to improve their properties, performances and advantages or by the blending of minor resin components to compensate the deficiencies of the main resin [6,7,8].

Amino resins are extensively used in coating systems. The amino resin is an optional constituent but plays the important role as a crosslinking agent to join molecules or functional groups of the other resin into a crosslinked network [8,9,10]. To achieve solubility in organic system, the melamine resin is combined with an alcohol such as *n*-butanol or methanol.

Transcript data about the study of alkyd-amino resins blend as a binder in protective coatings are not often published. Interest was more often committed to other resins blend. A study of several reviews of polymeric coatings with silicone modified alkyd resin has been done [5,6,7,8]. It has been observed that, when a 30% concentration of a ketone resin was blended to 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 [6,7,8].

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Butylated melamine formaldehyde resin as the cross-linker in a combination of alkyd, polyester, epoxy, blocked poly-isocyanates and an acrylic polyols give coatings with good chemical resistant properties [12,13]. A new four-step synthetic route for combining with melamine resin was developed and their uses for industrial applications was demonstrated [13,14].

The paper discusses the influence of the variation of butylated melamine formaldehyde and alkyd resin compositions on the properties of the coating-films. The formaldehyde releases 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 [9,10,11]. The properties of coatings are strongly dependent on film formation [10, 11,12]. If an alkyd resin is synthesized on the basis of “undry” oil (or saturated fatty acids) it is unable to form the coating film by itself but only in combination with other resins. 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 [14,15,16]..

A proper alkyd-amino resin blend is the standard composition for the preparation of coatings called “stoving or baking enamel”. The results of the effects of the alkyd-butylated melamine formaldehyde resin having weight ratio (from 80:20, 75:25, and 70:30 to 50:50) and the curing at elevated temperature (from 100 °C to 140 °C) for time periods of 20 to 35 minutes for the crosslinking, curing and superior properties of the coatings have been presented in this paper [13-16].

II. EXPERIMENTAL PROCEDURE

Rutile TiO_2, additives, solvents, amino resin, alkyd resin (containing 25 wt. % of saturated fatty acids produced by “Helios-Domzale”, used as a 70 % solution in methoxy propyl acetate), ball mill, and all other essential apparatus were provided by R&D Lab, ICI Paints Limited (Berger Paints) and Tata Motors Ltd. Jamshedpur during project work.

Paint Formulations and Applications: Paint preparation process was carried out in several steps. In 1st step, composition of micron sized TiO_2 pigment was determined keeping the view of pigment-binder ratio for optimum dispersion of pigments in alkyd-amino resins media during paint preparation. In 2nd step, mutual homogeny between alkyd and amino resins, i.e. consistency, transparency and adhesion of clear coat of each coating system were checked as per determined ratio (8:2, 7.5:2.5, 7:3 and 5:5) given in table 1.

Table 1. Determination of weight-percent ratio of alkyd-BMF resins for optimum mutual compatibility

Resin	**Wt. % ratio**	**Wt. % ratio**	**Wt. % ratio**	**Wt. % ratio**
Butylated MF resin	20	25	30	50
Alkyd resin	80	75	70	50

Table 2. Labeling of the formulated coatings as per alkyd-amino resins ratio

Alkyd-amino resins ratio	Labeling of paints as per alkyd-amino resins ratio with different curing temperature (°C) for **30 minutes.**				
- -	100° C	110° C	120°C	**130°C**	140° C
80:20	1a	1b	1c	1d	1e
75:25	2a	2b	2c	**2d**	2e
70:30	3a	3b	3c	3d	3e
50:50	4a	4b	4c	4d	4e

Alkyd and melamine resins were mixed in a dissolver. Then required solvents were added to control the viscosity. Experimental mild steel panels were cleaned and surface treated with a thin layer of phosphate coating, primer coat, and then the formulated paints were applied. Curing of coatings was carried out at temperatures from 100°C to 140 °C for 30 minutes. Then the sample-panels with coated films were left in laboratory for 24 hours at room temperature. The thickness of the dry coating film was 30-35 micron over the primer coat. The designations and the compositions of the samples have been presented in Table 2.

In 3rd step, a two litre ball mill was charged using superior grade chemical ingredients and sophisticated technology to prepare mill base for preparation of super white stoving top coats as per following calculated ingredients (given in table-3A).
For proper grinding & blending, the ball mill was run for 24 hours with below mentioned calculated chemicals to get particle size ≤ 1μm. Dispersion was checked using Hageman’s fine-Gauge and found particle size less than 5 micron. After that further quantity of MF resin and other solvents were added (given in table- 3B) and the ball mill was run again for 2 hours with said compositions and dropped in a pot. For complete extraction of mill base, butanol and C-IX were added in the mill (given in table- 3C) and again that was run for 30 minutes and dropped in a pot. Thus tables- 3A, 3B & 3C show different types of mill base raw materials having 44% by weight of required paint samples and by using these mill bases, different resins based paint formulations were done (mentioned in table-4).

Table 3 A. Preparation of mill bases with different ratio of alkyd- melamine formaldehyde resins

Composition	**Weight % ratio (in gram) × 20**	**Total weight**
Rutile TiO_2	23	460 gm
Butylated melamine formaldehyde resin	5	100 gm
Disperbyk additive	1	20.0 gm

Butanol	1	20.0 gm
Butyl cellosolve	1	20.0 gm
Xylene	1	20.0 gm
Solvent C-IX	1	20.0 gm
Nano byk (silica) additive	0.2	4.0 gm

Table 3 B. Blending of curing resin and solvents:

Composition	**% by weight (in gram) × 20**	**Total weight**
Butylated melamine formaldehyde resin	7× 20	140 gm
n-butanol	1× 20	20.0 gm
Solvent C-IX	1× 20	20.0 gm

Table 3 C. The let down stage; blending of organic solvents for complete extraction of mill base: -

Composition	**% by weight (in gram) x20**	**Total weight**
Butanol	0.8× 20	16.0 gm
Solvent C-IX	1× 20	20.0 gm
Total contents	44% each	880 gm each

Table 4. Make up stage for ultimate paint preparation

Composition: Alkyd-amino stoving paint	**% by weight (in gram) × 20**
Mill-base	44.0
Alkyd resin	43.0
Xylene	2.7
Butanol	2.0
Butyl cellosolve	1.0
Solvent C-IX	4.8
Methoxy propyl acetate	2.0
Slip additive	- -
Dispersion additive	0.2
Thixotrope	0.3
	Total 100%

In present study, 20 types of alkyd-amino paint coated sample no. 1a, 1b, 1c, 1d, 1e, 2a, 2b, …,4a,…., 4e have been characterized as under: pot life testing (there should be no pigment settlement, sedimentation, skinning and vehicle separation): viscosity, thinning ratio, non volatile contents, sagging, tack free & drying time, settling property, curing schedule, wrinkling test, dry film thickness (DFT), opacity, shade, gloss, impact test/cupping value test, hardness, salt spray test (corrosion test), Q.U.V. weathering resistance test etc according to the ASTM Standard for automotive paints [8, 9]. For proper application & excellent adhesion of paint film, surface treatment (i.e. degreasing, water-rinse, de-rusting, water-rinse, activation, phosphating and again water-rinse, passivation and drying) on standard mild steel panels has been done as per high quality automotive specifications [9]. Three coat systems (i.e. Electrodeposition primer, intermediate coat and top coat) were applied on surface treated mild steel panels and cured at 130±2°C for 30 minutes (set up optimum curing schedule) given in Table- 6.

Determination of the properties of dry coating films: the hardness of the coating film was determined by the standard method JUS H. C8.055 using a Koenig's pendulum. The bell-clapper was placed on a panel having coating film under an angle of 6 degree and left to oscillate. The elapsed time (in seconds) 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 Ericson's instrument for "deep drawing". A semi-sphere like cup hits a coated panel and performs "deeply drawing". The distance from the zero position of cup to the moment when the film cracks is defined as "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 determined diameter. During the specified time the coated film should not crack and peel off from the panel.

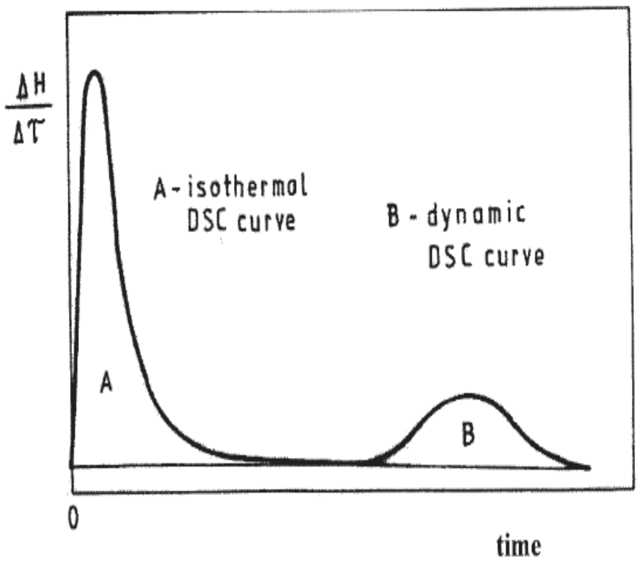

Figure 1. Classic DSC-thermogram of alkyd-amino resins blend curing (sample no. 2d; T = 130 °C, resins ratio 75:25)

The impact resistance was measured in accordance with the standard method JUS H.C8.050 using an Ericson's instrument with a weight falling spherical knob 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 x 1 mm) by cross-cutter. If none of them separate from the panel, the degree of film adherence is the best (that value is denoted as GT-0: 100/100). The gloss of the coating film was measured by "Glossometer"; an automatic instrument using an optical prism at an angle of 20 degree & 60 degrees to reflect the light from coated surface and it is digitally measured.

Determination the degree of curing: The degree of curing of the alkyd-amino resins blend was determined by differential scanning calorimeter (DSC), using a Du-Pont model-910 instrument, under isothermal conditions in the temperature range 100–140°C, and in the dynamic thermal range by further heating of the sample from the temperature of isothermal curing up to 140°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 160°C at a heating rate of 10°C/min. A typical DSC thermogram of resin curing is given in Figure 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 & 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.

III. RESULTS AND DISCUSSIONS

The determined properties of the dry coating films are given in table 5 & 6. Samples 3a and 4a (cured at a temperature of 100 °C) 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 minimum acceptable value for the hardness is 40 according to the standard method ASTM/BIS/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 minimum value for the drawing elasticity is 6 mm according to the standard JUS-C-T7-371. All the investigated coating films were satisfactory values (mostly between 9 and 10). The drawing elasticity decreases with increasing curing temperature but is independent of the resins 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 (approx 80 kg/cm^2). The values for the film adherence (GT-0 for all samples) and gloss (95 to 99%; minimum acceptable value is 80 %) were excellent.

Table 5. Assessment results of coating-films

Labeled specimens	Hardness	Drawing elasticity mm	Impact resistance kg/cm^2	Gloss /%
1a	28	7.8	55	90
1b	50	8.0	80	95
1c	71	9.0	81	95
1d	100	10.0	82	98
1e	127	10.	83	98
2a	29	10.0	60	91
2b	68	10.0	82	98
2c	99	9.0	83	98
2d	**121**	**10.0**	**87**	**99**
2e	141	9.9	82	99
3a	40	9.7	83	90
3b	110	9.8	83	98
3c	120	10	84	98
3d	130	9.8	84	99
3e	160	8.9	83	95
4a	41	7.0	83	90
4b	150	7.1	82	93
4c	155	7.5	81	95
4d	156	8.0	80	95
4e	185	6.1	79	95

On the basis of the obtained experimental results (table 5), and keeping into consideration of the economic factor, it can be seen that suitable coating properties could be achieved with an alkyd-melamine resins ratio of 75:25, a curing temperature of 130°C and a curing time of 30 minutes. Curing temperatures above 130°C are technologically unfavorable and unusable. 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 Tables 5 and 6. 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 increases with increasing ratio of melamine resin in resin blend and also with increasing the specified curing temperature.

Table 6. Effects of alkyd-melamine resin ratio and curing temperature on the degree of curing

Alkyd-amino resins ratio	Degree of curing (%)				
	100° C	110 °C	120 °C	**130 °C**	140°C
80:20	47	66	80	95	> 100%
75:25	48	68	85	**99**	> 1005
70:30	47	68	88	98	> 100%
50:50	49	69	90	98	> 100%

Schematic image of the chemical structures of conventional coating consist of alkyd-amino resins cross-linker and SEM image of rutile TiO_2 pigment based coating sample 2d with inserted image at higher magnification can be observed from figures 2 and 3 respectively.

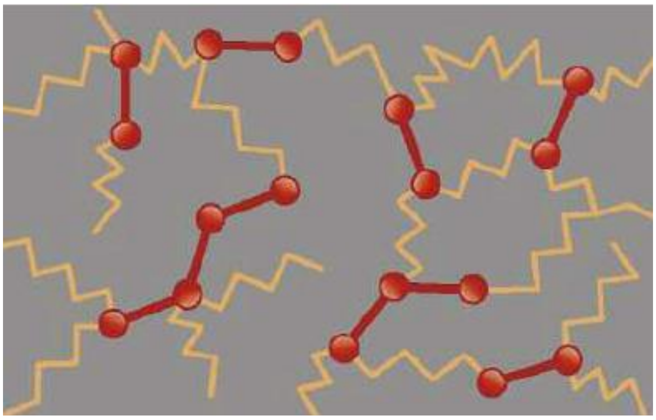

Figure 2. Schematic illustration of the chemical structures of the conventional coating consist of resin-cross-linker

SEM characterization of TiO_2 pigment based coatings

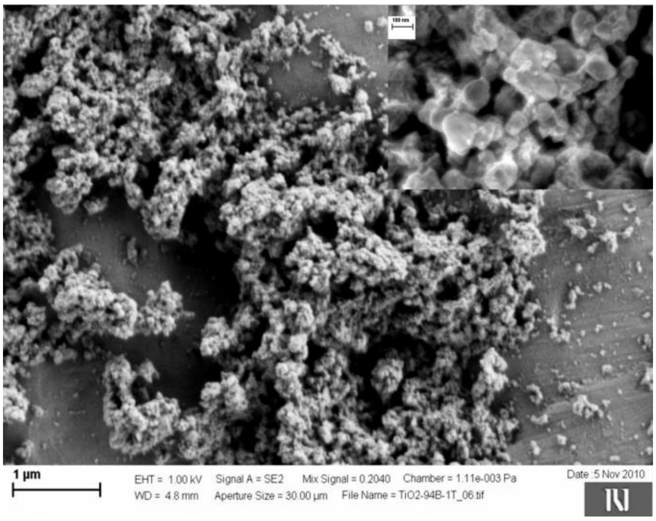

Figure 3: SEM image of coating sample with inserted image at higher magnification

A noteworthy increase in the hardness of the coating films with increasing of both above-mentioned parameters was shown in this investigation, so the degree of curing has a prominent effect on the hardness of the obtained film [16,17].

IV. CONCLUSIONS

The significance of the ratio (80:20, 75:25, 70:30 and 50:50) of alkyd-amino resins, curing temperature (from 100°C to 140°C for 30 minutes) for the purpose of crosslinking reactions, and the difference in performances of the coatings have been explored. The assessment of the degree of crosslinking reactions between functional groups of alkyd and amino resins has been studied. The adhesion property, gloss, hardness, elasticity, impact resistance have also been evaluated.

Best possible performance in the curing processes of coatings have been studied with a ratio (75:25) of alkyd-amino resins and at a curing temperature of 130±2°C and curing time of 30 minutes. 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 minutes.

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REFERENCES

[1] Frank N. Jones (2005), "Alkyd Resins", Ullmann's Encyclopedia of Industrial Chemistry, Weinheim: Wiley-VCH, doi: 10. 1002/ 14356007; 401-409. Jan.2003.
[2] http://www.indiamart.com/paganpaints-chemicals/automotive-industrial-paints.html#polyurethane-paint-primier.
[3] http://www.grauerandweil.com/automotive-general-industrial-paints.html.
[4] http://www.grauerandweil.com/automotive-general-industrial-paints.html.
[5] V. V. Verkholantsev, Eur. Coating J. 12 (1998) 942.
[6] Y. Nakayama, Prog. Org. Coating. 33 (1998) 108.
[7] Modern Plastics Encyclopedia Handbook, Modern Plastics Magazine, Mc Graw-Hill Inc., New York, 2000.
[8] W. D. Ho, C. C. M. Ma, Infrared Phys. Technol. 38 (1997) 123.
[9] C. Carr, E. Walstom, Prog. Org. Coat. 28 (1996) 161.
[10] W. D. Athawale, A. V. Chamankar, J. Am. Oil Chem. Soc. 75 (1998) 887.
[11] Z. A. He, W. J. Blank, J. Coating Technol. 71 (1999) 85.
[12] J. Mahler, G. Rafler, Optical Materials 12 (1999) 363.
[13] P. Kalenda, A. Kalendova, JOCCA-Surface Coatings International 78 (1995) 508.
[14] A. Hofland, ACS Symposium Series 663 (1997) 183.
[15] K. Saunders, Organic Polymer Chemistry, Chapman and Hall Ltd., London, 1973.
[16] R. Radi~evi}, D. Stoiljkovi}, J. Budinski-Simendi}, J. Therm. Anal. Cal. 62 (2000) 237.
[17] G. O. Young, "Synthetic structure of industrial plastics (Book style with paper title and editor)," in Plastics, 2nd ed. vol. 3, J. Peters, Ed. New York: McGraw-Hill, 1964, pp. 15–64.

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