Acrylate Grafted Dehydrated Castor Oil Alkyd—A Binder for Exterior Paints

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To meet the requirement of improved durability of alkyd resin for use in weatherwork paint for superstructure of ships, an attempt has been made to chemically modify a castor oil alkyd by graft copolymerization with methyl methacrylate and butyl methacrylate in view of their ability to provide polymers with good exterior durability. Characterization of the experimental resins, in respect to physical properties, was carried out using instruments such as a vapor pressure osmometer, rotational viscometer, universal tensile testing instrument (Instron 1123), and differential scanning calorimeter. Performance of the resins was evaluated using a fluorescent UV accelerated weatherometer and multi-head glossmeter.

The results reveal substantial improvement in drying and weather resistance properties of castor oil alkyd on graft copolymerization with both methyl methacrylate and butyl methacrylate. The improvement in these properties is marginally superior in the case of MMA grafted alkyds. MMA modification also enhances the mechanical properties of the grafted castor oil alkyd.

INTRODUCTION

Alkyd resins are used extensively as a binder for making exterior paints. This paint is applied on the superstructure of ships and remains exposed to UV radiation, thermal fluctuations, high humidity, and wind driven salt spray. Under such extreme conditions of marine atmosphere in the Indian tropical region, it shows considerable chalking, color fading, and loss of gloss within a period of 9-12 months. One way to increase the durability and enhance the service life of the exterior paint is to improve weather resistance through chemical modification of alkyd with urethane, silicone, vinyl, and acrylic resins.[1] This offers the possibility of combining the ease of application and film forming properties of alkyd with the exterior durability of vinyl and acrylic system due to their resistance to hydrolysis and UV degradation.[2]

The modification of alkyd resins by acrylation for improving their properties has been extensively investigated. Various methods have been employed by researchers for such chemical modifications. A method for the synthesis of acrylated alkyd was first attempted by F. Armitage and S. Kut.[3] Methods of synthesis of acrylate modified alkyd using esterification reaction between anhydride, carboxyl, or epoxide groups in preformed copolymer and hydroxyl and carboxyl groups of alkyds have been extensively reported by D.H. Solomon and co-workers.[4-7] Fletcher et. al[5] suggested a method involving reaction between a carboxyl group containing acrylic copolymer and a monoglyceride followed by polyol and dibasic acid to achieve further condensation. An alternative method for alkyd modification is the post-vinylation of resin with vinyl/acrylic monomers. This method involves the grafting of an acrylate segment to an unsaturated fatty acid in an alkyd resin through free radical chain polymerization.

Styrene and vinyl toluene have also been used for the modification of alkyds for improving their properties.[8-10] Such modifications provide alkyds with better color and improved drying characteristics as well as water and alkali resistance properties. These modified alkyds are applied mostly in very rapid air drying and low temperature baking finishes for industrial use. However, these modified alkyds have not been used for weatherwork paints of ships in view of poor resistance to weathering.[11] Further, styrenated alkyds require aromatic solvents and are not suitable for brushing finishes in view of their rapid drying properties. The paints for

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Table 1—Composition of Acrylated DCO Alkyd Resins

Composition	Concentration (% by wt) Alkyd	MMA	BMA
MA 1	80	20	—
MA 2	70	30	—
MA 3	60	40	—
MA 4	50	50	—
BA 1	80	—	20
BA 2	70	—	30
BA 3	60	—	40
BA 4	50	—	50

superstructure of ships are required to be brush applicable.

This paper reports on a study related to the modification of dehydrated castor oil (DCO) based alkyd resin by graft copolymerization with acrylate monomers. The aim of this work is to develop a suitable binder to formulate high performance exterior paints for use on marine platforms under tropical conditions. Therefore, methyl methacrylate (MMA) and butyl methacrylate (BMA) monomers were used in the study as they are reported to provide polymers with very good exterior durability compared to other conventional monomers.[2] In earlier literature,[4-7] improvement in the performance of acrylated alkyd films in comparison to unmodified alkyd films has been reported through qualitative testing of abrasion resistance, impact resistance, and humidity resistance. However, any information regarding the effect of weathering on gloss and mechanical properties of the films is scarcely available. This paper reports the improvement in performance of acrylated alkyd film focusing on the effect of weathering on gloss and mechanical properties.

Table 2—Molecular Weight and Viscosity of MMA Modified Alkyd Resins

Composition	Characteristics Molecular Weight	Viscosity at 30°C
Alkyd	2930	1069
MA 1	3700	904
MA 2	4950	868
MA 3	5796	764
MA 4	5940	687

Table 3—Drying Property of Acrylated DCO Alkyd Resins

Composition	Characteristics Hard Drying Time, hr	Nature of Dry Film
Alkyd	8	Tacky
MA 1	2	Tackfree
MA 2	1.5	Tackfree
MA 3	1.5	Tackfree
MA 4	1	Tackfree
BA 1	3.5	Tacky
BA 2	2.5	Tackfree
BA 3	2.0	Tackfree
BA 4	1.5	Tackfree

EXPERIMENTAL

Chemicals

The resin and all the reagents were used as received. Commercial grade DCO alkyd resin of oil length 55% and solid content 50% was used. AR grade of acrylic monomers methyl methacrylate, butyl methacrylate, and the initiator Di-t-butyl peroxide were obtained from Fluka Chemical, Germany. Benzyl alcohol - LR grade was supplied by E. Merck (I) Ltd.

Synthesis of Acrylated Alkyd

Two series of modified DCO alkyd resins were prepared using MMA and BMA in concentrations varying from 20 to 50% of solid alkyd resin. Compositions of modified alkyd resins are given in *Table* 1.

Alkyd resin and benzyl alcohol were heated together at 90-120°C for 30 min with continuous stirring in a four-necked flask fitted with a reflux condenser, thermometer, inlet tub, and stirrer. The monomer, premixed with the initiator (0.85% of the alkyd solid), was introduced into the reaction mixture gradually over a period of three to four hours maintaining the temperature at 90-120°C in an inert atmosphere of nitrogen. After complete addition of the monomer, the reactants were held at the same temperature for six to eight hours. When the solid content of the mixture reached the theoretically calculated value, the reaction mixture was cooled to room temperature.

Characterization of Acrylated Alkyd Resins

The experimental acrylated DCO alkyds were examined for iodine value, molecular weight, and viscosity using standard methods. For these determinations, MMA homopolymer was separated from the resin solution through precipitation using petroleum ether (60/80). The unreacted monomer and solvent were removed by drying under vacuum. The iodine value of the alkyd and 40% MMA grafted alkyd were measured employing ASTM D 1959.[12] Viscosity measurements were carried out with 50% alkyd solution in xylene (w/v) at 30°C using Haake Rotovisco RV 3 in accordance with the method described in British specification[13] at a shear rate of 1000 sec^{-1}. The average molecular weight of the modified alkyds was determined using the resin solution after diluting it in xylene at four different concentrations with a vapor pressure osmometer (Knauer Berlin 37) using Benzil as calibration standard.

Performance Evaluation of Acrylated Alkyd Films

Film characteristics of modified DCO alkyds have been evaluated to ascertain the improvement in properties of alkyd as a result of acrylic modification. For the following tests the acrylated alkyd resins were used as synthesized, without removing homopolymers. However, a requisite amount of driers was added to facilitate drying of the resin films.

The drying time of alkyd resin was determined by applying it to clean, degreased tin panels (127 × 50 mm)

and examining the film condition as per Indian specification.[14]

Free films of alkyd and modified alkyd resins were prepared using a motorized film applicator on glass plates precoated with methyl cellulose. First, one coat of resin solution was applied using a 250 μm applicator which was allowed to dry for 24 hr. Thereafter, the second coat of resin was applied employing a 300 microns applicator. The coated panels were stored in a dust free chamber for proper drying of the alkyd film. After 15 days of drying, the films were peeled off from the plates, washed thoroughly under running water to remove cellulose film, and dried at an ambient temperature.

Water vapor permeability measurements were carried out gravimetrically as per method described in ASTM D 1653.[15] Determination and average values were made using standard Payne cups of 10 cm^2 area in quadruplicate. Tensile strength and elongation properties of the film were determined as per the method given in ASTM D 882.[16] The test specimens were cut from cured film in the form of stripes measuring 100 × 15 mm in size and were conditioned at 50% relative humidity for 24 hr before examination using the Universal tensile testing instrument (Instron 1123) under strain rate of 20 mm/min. Ten specimens were examined for each composition and the average result of the six highest readings at peak load was reported as tensile strength. The strain values at the breaking point were used to obtain percent elongation.

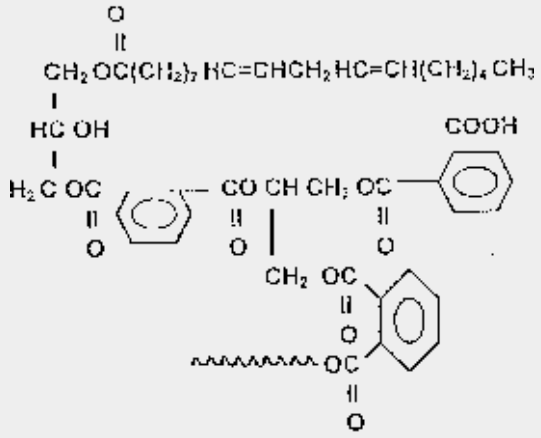
Weathering resistance of acrylated DCO alkyd was examined by exposing the resin coated aluminum panels (150 × 75 mm) to UV radiation (wavelength 285-315 nm) and high humidity condition in QUV accelerated Weatherometer.[17] A cycle comprised of four hours of UV exposure (temperature 60 ± 5°C) and two hours of condensation (temperature 45 ± 5°C) was maintained during the study. Gloss measurements, initial and after weathering, were carried out by the method described in British specification[18] using multi-head glossmeter at 20°.

Glass transition temperature (T_g) of MMA modified alkyd resins was examined with a differential scanning calorimeter (DuPont 910) using resin films cured for 15 days.

RESULTS AND DISCUSSION

A typical structure of DCO alkyd is shown in *Scheme* 1. In the DCO alkyd, besides the sites of unsaturation in fatty acid chains, graft copolymerization can be initiated on the active methylene group through hydrogen abstraction in presence of an initiator like di-t-butylperoxide. It initiates polymerization of the monomer to produce branches by grafting from mechanism (*Scheme* 2).

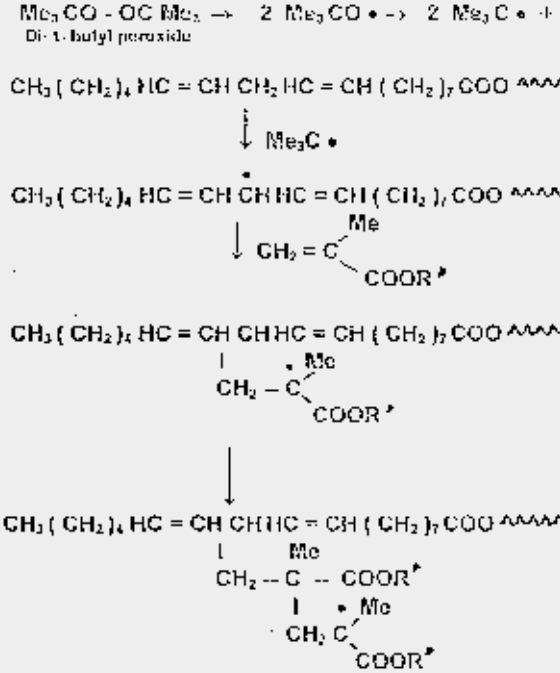
The measured iodine values of the parent alkyd and 40% MMA grafted alkyd are 72 and 43 g of I_2 per gram of resin, respectively. The theoretical iodine value of 40% modified alkyd comes to 43.2 gms of I_2 per gm of resin (72 × 60/100 = 43.2). This suggests no loss of unsaturation in alkyd during grafting providing support in favor



Scheme 1

of grafting from mechanism (*Scheme* 2) for the formation of acrylated alkyd.

Results in *Table* 2 show that on modification with methacrylates, molecular weight of DCO alkyd increases with a simultaneous decrease in solution viscosity. An increase in molecular weight normally leads to an increase in viscosity for linear chain polymers. On the other hand, for the same molecular weight, a branched polymer has a lower viscosity compared to a linear polymer, due to the introduction of stiffness and compact-



Scheme 2

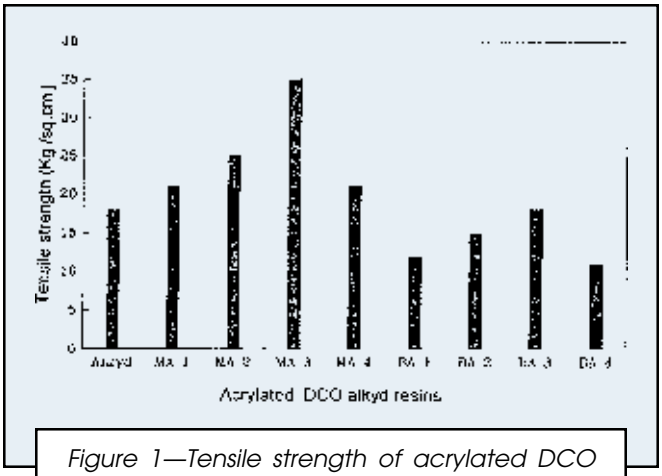


Figure 1—Tensile strength of acrylated DCO alkyd resins.

Table 4—Water Vapor Permeability of Acrylated DCO Alkyd Resins

	Water Vapor Permeability (mgm.mm/sq. cm./day)		
Composition	**Initial**	**After 3 Months**	**After 6 Months**
Alkyd	0.43	0.40	0.37
MA 1	0.39	0.35	0.33
MA 2	0.37	0.34	0.32
MA 3	0.30	0.25	0.23
MA 4	0.30	0.24	0.21
BA 1	0.40	0.36	0.34
BA 2	0.39	0.33	0.31
BA 3	0.36	0.31	0.27
BA 4	0.32	0.28	0.26

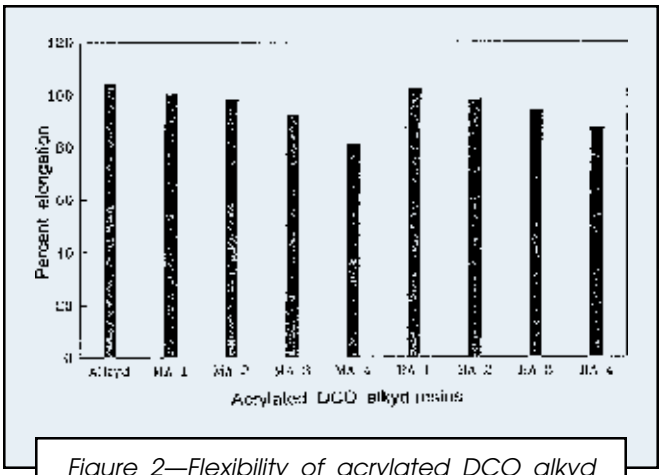


Figure 2—Flexibility of acrylated DCO alkyd resins.

Table 5—Glass Transition Temperature of MMA Modified Alkyd Films

Composition	**Glass Transition Temp. (T_g)°C**
Alkyd	12
MA 1	20
MA 2	32
MA 3	54
MA 4	25 & 26

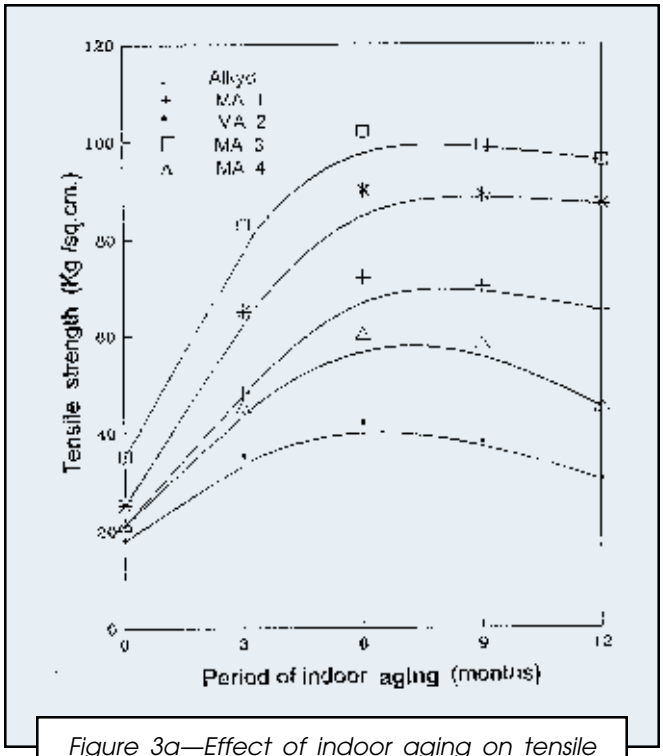


Figure 3a—Effect of indoor aging on tensile strength of MMA modified DCO alkyd resin films. •—alkyd; +—MA 1; ⋆—MA 2; ❑—MA 3; and Δ—MA 4.

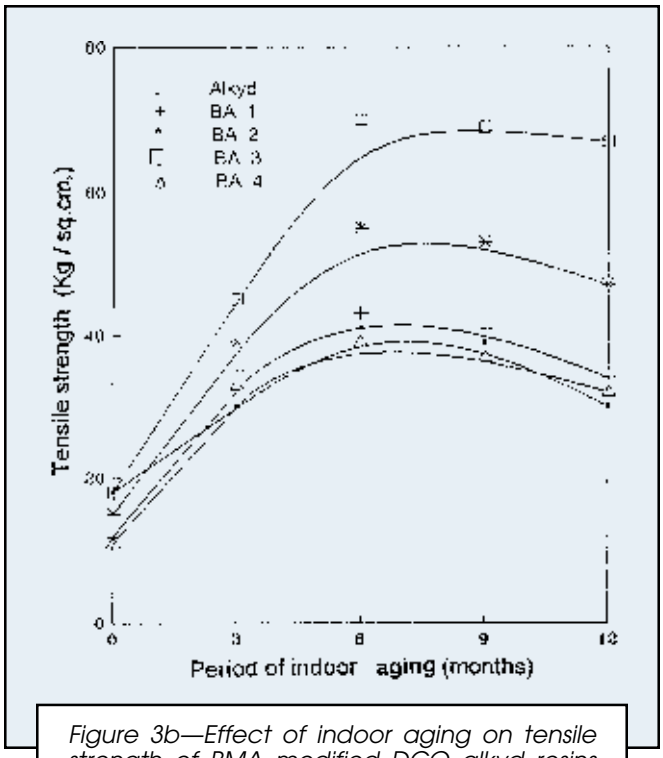


Figure 3b—Effect of indoor aging on tensile strength of BMA modified DCO alkyd resins films. •—alkyd; +—BA 1; ⋆—BA 2; ❑—BA 3; and Δ—BA 4.

ness in the molecule by branches.[19] In the present case, the branches are chemically different from the main chain. The introduction of such branches has definitely increased molecular weight of the parent alkyd polymer but has resulted in considerable compactness. This seems to have overshadowed the influence of molecular weight increase, thereby decreasing the viscosity considerably.

Significant improvements in the drying property of the alkyd resins have been observed as a result of modification with acrylates. It has been found that drying time decreases with an increase in acrylic content, being minimum at 50% modification for both types of acrylate monomers (*Table* 3). Incorporation of MMA produces tack free films by modification at all concentrations, whereas BMA is effective at 30-50% concentration.

Water vapor permeability of alkyd resin films (thickness 90-100 μ) was measured in quadruplicate using Payne Cups of 10 cm^2 area. Permeation of water vapor from higher to lower concentration is governed by the kinetics of movement of absorbed water molecules under its vapor pressure gradient. With the increased incorporation of acrylates into the alkyd main chain through grafting the intramolecular packing of the alkyd chain increases, which reduces the rate of water vapor permeation through resin films[20] (*Table* 4). Similar studies were conducted with films weathered under normal laboratory conditions for three to six months. A gradual decrease in water vapor permeation has been recorded with the increase in period of indoor aging (*Table* 4). Further polymerization accompanied with crosslinking of the resin molecules is perhaps responsible for restricted migration of water vapor through weathered films.

Mechanical properties of modified DCO alkyd resins were evaluated by determining the tensile strength and elongation of the free films. These characteristics were also determined after aging the films indoor for one year in the laboratory as well as after exposure to accelerated weathering conditions. It can be seen from *Figure* 1 that the tensile strength of the acrylated alkyd resin film increases steadily with an increase in the MMA content of the alkyd up to the level of 40% modification. Contrary to this, modification with BMA causes reduction in the tensile strength of alkyd films. However, the value increases with BMA content, attaining the tensile strength equivalent to unmodified alkyd, at 40% concentration. Incorporation of BMA causes a plasticization effect in the alkyd due to the presence of bulky side groups. The increase in tensile strength with MMA modification can be ascribed to the increase in the cohesive strength of the molecules due to the formation of dense intermolecular packing as a result of intermingling of branches through grafting of MMA to the alkyd chain. Beyond the 40% level of modification, the formation of high proportion of homopolymer causes phase separation from the grafted alkyd and results in lower tensile strength of the resin films.

A similar effect can be observed in the case of T_g of acrylated alkyd which increases with the acrylate content (*Table* 5) due to the formation of a compact microstructure through the intermingling of branches. At a 50% modification level, glass transition occurs at two temperatures, 25° and 60°C, indicating phase separation

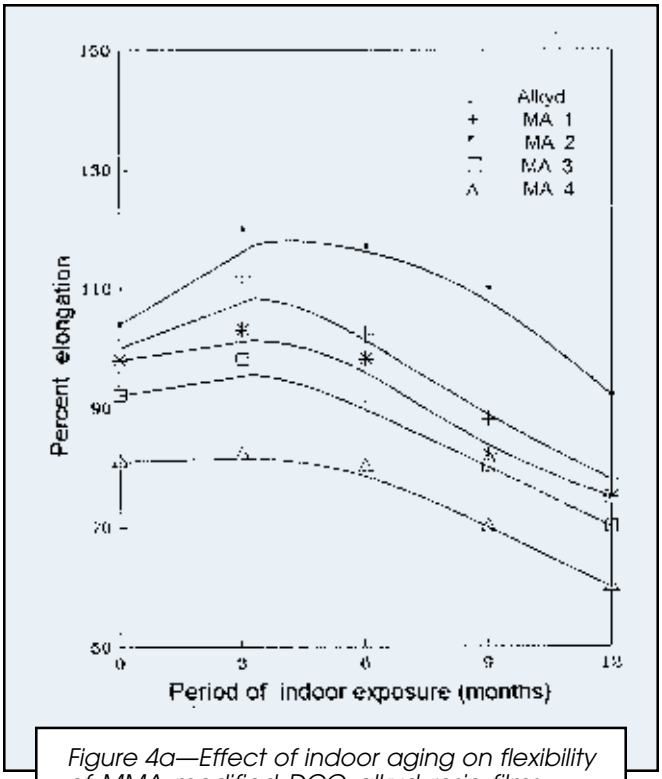


Figure 4a—Effect of indoor aging on flexibility of MMA modified DCO alkyd resin films. •—alkyd; +—MA 1; ⋆—MA 2; ❑—MA 3; and Δ—MA 4.

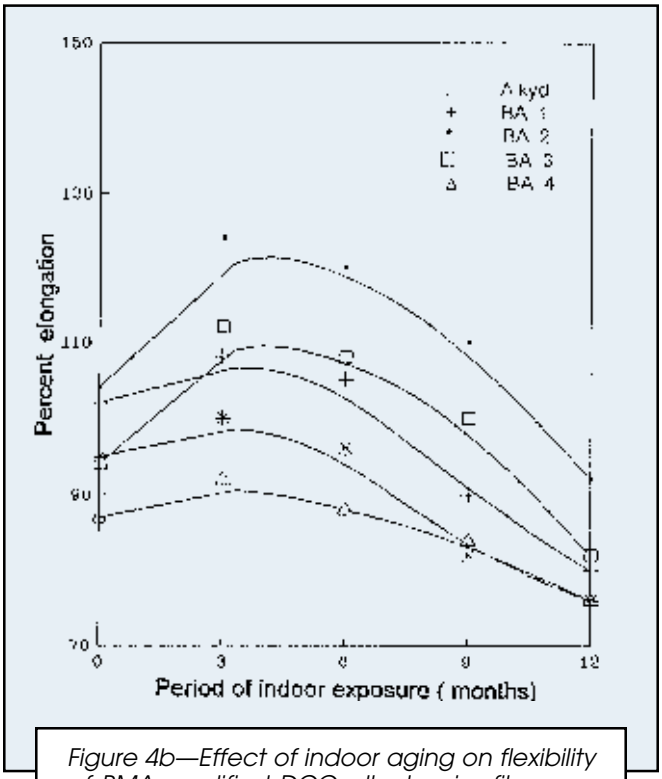


Figure 4b—Effect of indoor aging on flexibility of BMA modified DCO alkyd resins films. •—alkyd; +—BA 1; ⋆—BA 2; ❑—BA 3; and Δ—BA 4.

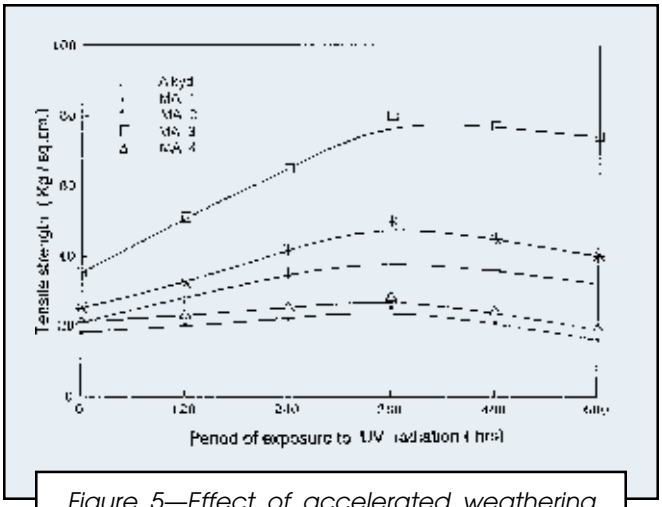


Figure 5—Effect of accelerated weathering on tensile strength of MMA modified DCO alkyd resin films. •—alkyd; +—MA 1; ⋆—MA 2; ❑—MA 3; and Δ—MA 4.

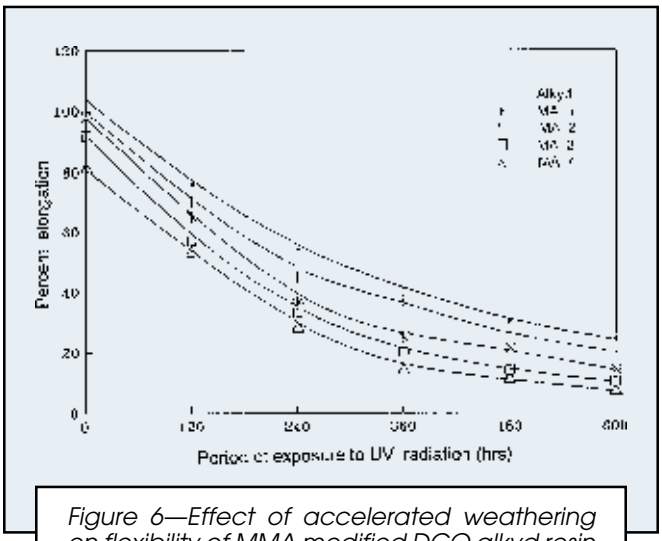


Figure 6—Effect of accelerated weathering on flexibility of MMA modified DCO alkyd resin films. •—alkyd; +—MA 1; ⋆—MA 2; ❑—MA 3; and Δ—MA 4.

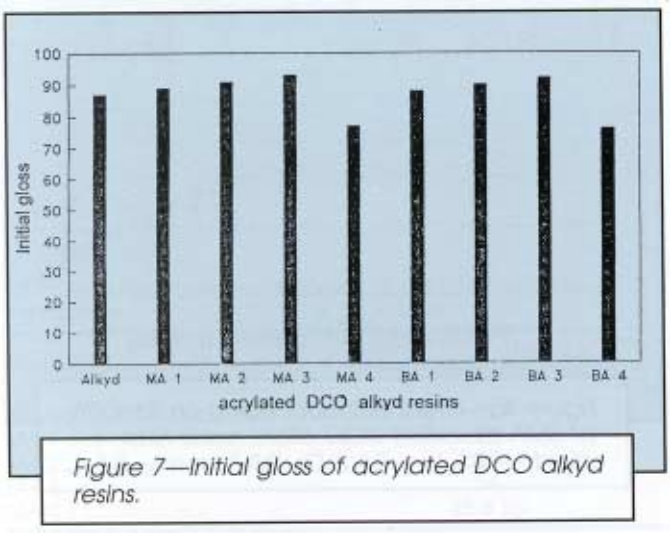


Figure 7—Initial gloss of acrylated DCO alkyd resins.

of homopolymer and grafted alkyd due to the formation of a large quantity of homopolymer.

On exposure of alkyd films to diffused light under indoor conditions, tensile strength steadily increases for six months followed by a very slow decrease during extended aging (*Figures* 3a and 3b). The initial increase in tensile strength for six months is attributed to the progressive crosslinking of alkyd molecules on exposure followed by degradation reactions causing a decrease in tensile strength. Among all the MMA modified alkyds, MA 3 resin possesses the maximum tensile strength, which is maintained even after 12 months of exposure.

Flexibility of alkyd resins generally decreases as a result of acrylate modification (*Figure* 2). The extent of decrease of percent elongation is greater for the MMA modified alkyd than that of the BMA modified alkyd. Flexibility increases during the initial three months of indoor aging, but decreases steadily thereafter (*Figures* 4a and 4b). This phenomenon is presumably due to build up of internal stresses caused by dimensional changes on prolonged exposure. Similar behavior has also been reported by Raju et al.[21] during their studies of indoor weathering on unpigmented alkyd films. As a matter of fact, substantiative yellowing was observed on the film after six months of aging, suggesting degradation of alkyd molecules.

Mechanical properties of the films exposed to the accelerated weatherometer were recorded at an exposure interval of 120 hr. It can be seen from *Figure* 5 that accelerated weathering leads to an increase in tensile strength of MMA modified alkyd resins up to 360 hr and is then followed by a gradual decrease. The resin with 40% MMA (MA 3) maintains a higher tensile strength during exposure as previously shown in indoor weathering experiments. Flexibility of the resins decreases steadily (*Figure* 6), as was observed in natural weathering, except for some initial changes which could be due to intense UV radiation, high humidity, and elevated temperature conditions maintained in the accelerated weatherometer which are not available in natural weathering.

Ability of a coating to retain its desired gloss during service is of great significance for maintaining an aesthetic appearance of the painted surface for longer periods. Acrylated alkyd resins synthesized in the present work were examined for their gloss retention characteristics by exposing resin coated aluminum panels in a QUV accelerated weatherometer. Initial gloss of coated panels and gloss values during weathering were measured every 100 hr for a total of 600 hr using a glossmeter at a 20° angle. Initial gloss of the resins has been improved up to 40% modification with both acrylates. Furthermore, increase in acrylic content led to a decrease in gloss which may be due to phase separation between the homopolymer and grafted alkyd, as discussed earlier (*Figure* 7). It can be seen from *Figures* 8a and 8b that on exposure to accelerated weathering, gloss retention property improves with an increase in acrylic content of the alkyd, maximum being at 40% level. At the end of 600-hr exposure, the acrylated alkyd with 40% acrylate content has a gloss value almost double to that of the unmodified alkyd.

CONCLUSION

Significant improvements have been observed in properties of DCO alkyd resin after modification with acrylates. The performance of the MMA modified alkyds has been found to be better than BMA modified alkyds. After modification with MMA, the glass transition temperature of alkyd has increased, resulting in improvement of drying time and mechanical properties of alkyd. Further, MMA modified alkyds possess better weather resistance compared to BMA modified resins. It is also concluded that incorporation of methyl methacrylate into the DCO alkyd in the range of 30-40% yields a binder suitable for formulation of high performance exterior paints. Beyond this level of modification, properties of the alkyd deteriorate due to phase separation of the homopolymer and grafted alkyd.

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References

(1) Lambourne, R., *Paint and Surface Coatings, Theory and Practice*, Ellis Harwood Ltd., London, p. 60, 1987.
(2) Oldring, P. and Hayward, G., *Resins for Surface Coatings*, Vol. 1, p. 177 & Vol. 2, p. 121, SITA Ltd., London, 1987.
(3) Armitage, F. and Kut, S., *J. Oil & Colour Chemists' Assoc.*, 35, 195 (1952).
(4) Solomon, D.H., *J. Oil & Colour Chemists' Assoc.*, 45, 88 (1962).
(5) Fletcher, J.R., Kelly, J.P., and Solomon, D.H., *J. Oil & Colour Chemists' Assoc.*, 46, 127 (1963).
(6) Hopwood, J.J., Pallaghy, C., and Solomon, D.H., *J. Oil & Colour Chemists' Assoc.*, 47, 289 (1964).
(7) Solomon, D.H. and Wigney, P.J., *J. Oil & Colour Chemists' Assoc.*, 48, 440 (1965).
(8) Hewitt, D.H. and Armitage, F., *J. Oil & Colour Chemists' Assoc.*, 29, 109 (1946).
(9) Redknap, R.F., *J. Oil & Colour Chemists' Assoc.*, 43, 260 (1960).
(10) Kovacs, L. and Charlesworth, D., *J. Oil & Colour Chemists' Assoc.*, 46, 47 (1963).
(11) Payne, H.F., *Organic Coating Technology*, Vol. 1, John Wiley, p. 304, 1965.
(12) ASTM D 1959: Test Method for Iodine Value of Drying Oils and Fatty Acids, *Annual Book of ASTM Standards*, Vol. 06.03, American Society for Testing and Materials, West Conshohocken, PA 19428.
(13) BS:3900 (Part A7), Determination of the Viscosity of Paint at a High Rate of Shear, British Standards Institution, 1968.
(14) IS:101 (Part 3/Sec. 1), Methods of Sampling and Test for Paints, Varnishes and Related Products. Part 3. Tests on Paint Film Formation, Sec. 1, Drying Time, Bureau of Indian Standards, 1986.
(15) ASTM D 1653, Test Method for Water Vapor Permeability of Organic Coating Films, *Annual Book of ASTM Standards*, Vol. 06.01, American Society for Testing and Materials, West Conshohocken, PA.
(16) ASTM D 882, Test Methods for Tensile Properties of Thin Plastic Sheeting, *Annual Book of ASTM Standards*, Vol. 08.01, American Society for Testing and Materials, West Conshohocken, PA.
(17) ASTM G 53, Practice for Operating Light- and Water-Exposure Apparatus (Flourescent UV-Condensation Type) for Exposure of Nonmetallic Materials, *Annual Book of ASTM Standards*, Vol. 14.02, American Society for Testing Materials, West Conshohocken, PA.
(18) BS:3900 (Part D5), Measurement of Specular Gloss of Non-Metallic Films at 20°, 60°, and 85°, British Standards Institution, 1980.
(19) Holmberg, K., *High Solids Alkyd Resins*, Marcel Dekker, p. 39, 1987.
(20) Sabra, A., Lam, T.M., Pascault, J.P., Loustalot, M.F.G., and Grenier, P., *Polymer*, 28, 1030 (1987).
(21) Raju, K.V.S.N. and Yaseen, M., *J. Oil & Colour Chemists' Assoc.*, 65, 401, (1982).

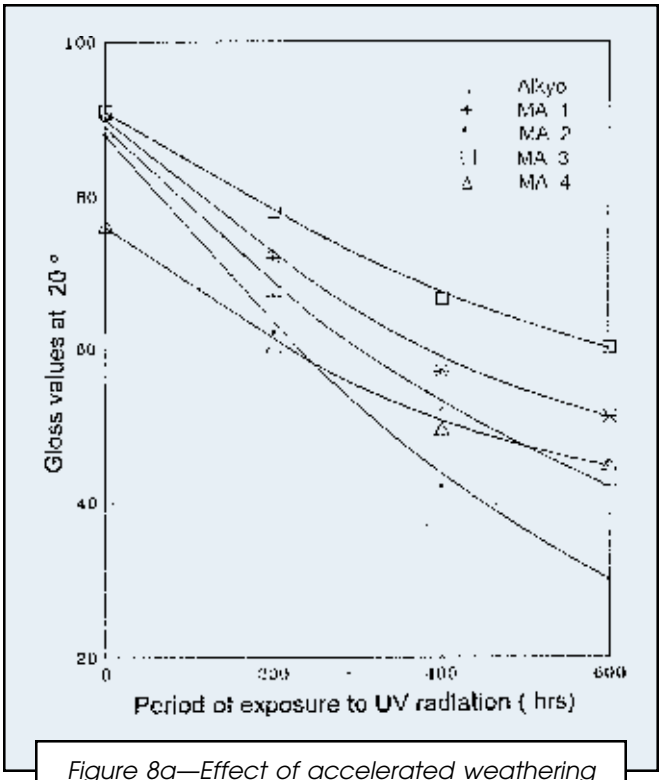

Figure 8a—Effect of accelerated weathering on gloss retention of MMA modified DCO alkyd resins. •—alkyd; +—MA 1; ⋆—MA 2; ❑—MA 3; and Δ—MA 4.

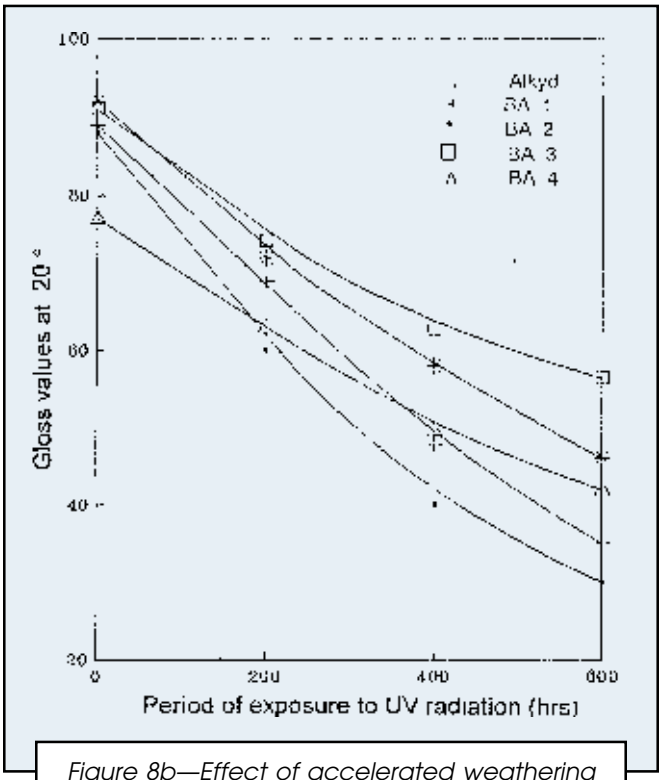

Figure 8b—Effect of accelerated weathering on gloss retention of BMA modified DCO alkyd resins. •—alkyd; +—BA 1; ⋆—BA 2; ❑—BA 3; and Δ—BA 4.