

Water Soluble Binder System from Malenized Argemone Oil

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Argemone oil has been malenized at 210°C using five different mole ratios of oil and maleic anhydride till desirable acid value of the resultant product is achieved. The malenized products have been neutralized with triethyl amineto make them water compatible. These water compatible products are blended with hexamethoxy methyl melamine (HMMM) in different ratios to prepare water based stoving compositions. Certain compositions are found to have comparable performance to that of the conventional water based alkyd-HMMM compositions when they are tested for their film and other properties.

Introduction

Water Based Coatings

The economic and environmental constraints and legislative restrictions have diverted the paint industry to develop water-based coating formulations. Water-borne coatings are finding more importance both for decorative and industrial coating applications. The environment conscious western world is doing a lot of research work on promotion and utilization of water thinnable coatings.

The main advantage¹ of using water as solvent that it is non-toxic and non-flammable. This aspects of water-borne systems means reduced insurance premium. It also alleviates odour problems and lowers the energy requirements for curing due to reduced air flow through the ovens.

Based on the type of resin/binders used in the water-borne coating formulations, they can be classified into three main groups:

- (i) Water-soluble or reducible,
- (ii) Colloidal or water solubilized dispersions, and
- (iii) Aqueous dispersions or emulsions.

Water Thinnable Vegetable Oils

Malenized oils are among the most important synthetic drying oil products because malenization consti-

tutes rather simple method for drying and semidrying oil modification in which free acid groups are introduced in the middle of an unsaturated chain to increase functionality. It is well known² that malenized drying oils produce water-reducible formulations for coatings. Maleic anhydride is reacted with unsaturation in oils to produce maleic adduct having pendent acid group which can be neutralized with ammonia or amines to produce water soluble oils as per illustrated scheme (Figure 1).

The applications of malenized oils in water based coating formulations has been reported in literature.³⁻⁸

Argemone oil⁹ is nauseous bitter non-edible (toxic) oil obtained from seeds of *Argemone mexicana*, an American plant which has run wild in India and is now a troublesome weed. The oil in view of its semidrying nature and high linoleic acid content (of around 60 per cent) can be maleic modified for possible value added utilization in water based coating formulations and hence it was thought appropriate to undertake the present work.

Experimental Procedure

Materials

The locally purchased argemone oil was analysed for physico-chemical characteristics by standard BIS methods¹⁰ (Table 1). The fatty acid composition of argemone oil was determined by gas liquid chromatography (GLC) of methyl esters¹¹ using a stainless steel column (2m x 0.32 mm) packed with 15 per cent DEGA at 185°C with nitrogen as a carrier gas at a flow rate of 30 ml/min us-

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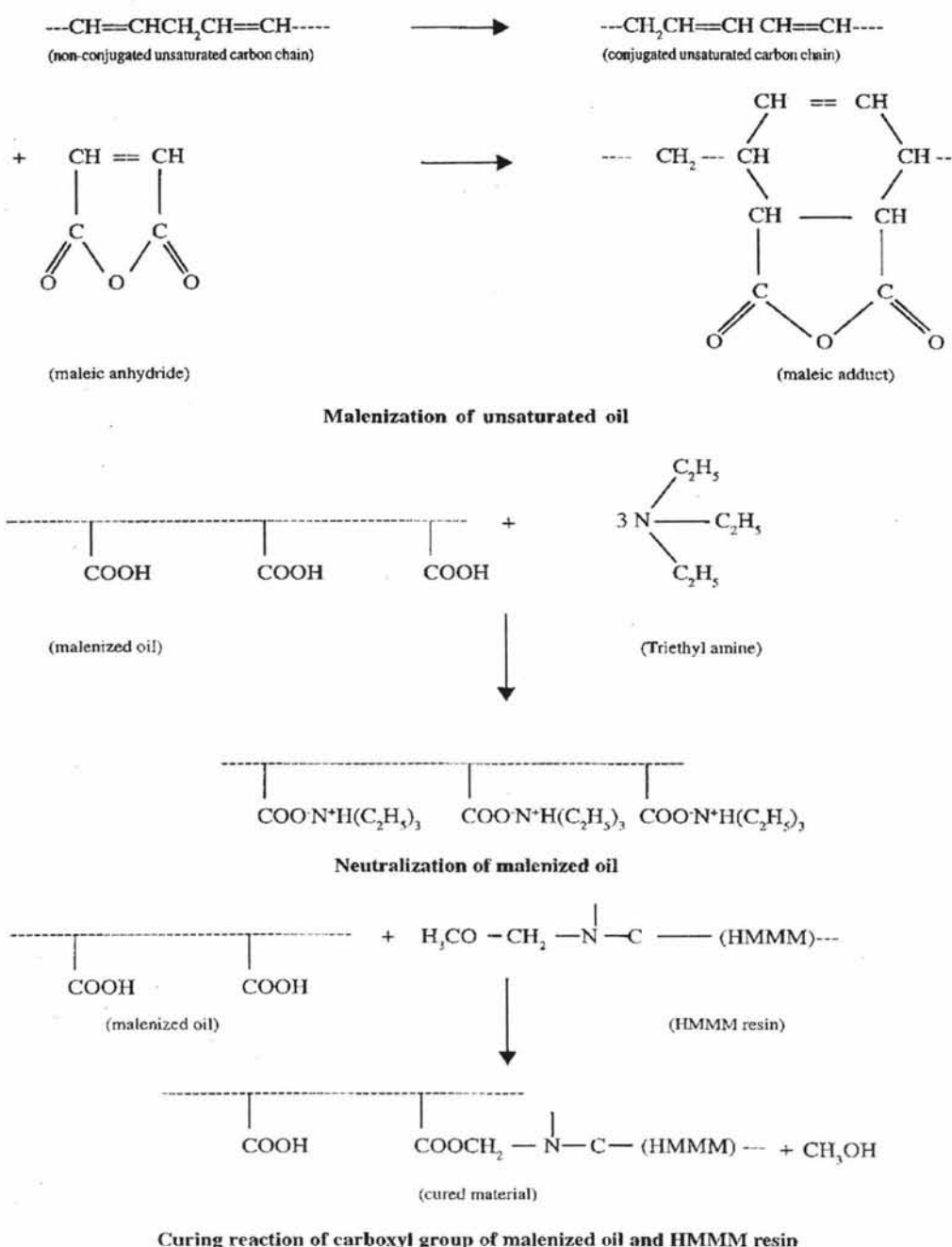


Figure 1— Reactions scheme of malenization, neutralization and curing

ing flame ionization detector at an injector temperature of 220 °C (Table 2, Figure 2).

The water soluble melamine resin (HMMM) was procured from M/S Pidilite Industries, Vapi (Gujarat). The physical properties of HMMM are reported (Table 3). The commercial grade of conventional water soluble alkyd (CWSA) to be used as reference for comparison

was locally purchased and analysed for physical properties as per BIS methods¹² (Table 4). Other materials were of laboratory grade.

Malenization of Argemone Oil

Oil and maleic anhydride¹³ were taken in three neck flask equipped with heating and stirring arrangement. The malenization reaction was carried out at 200- 210°C

Table 1— Physico-chemical characteristics of argemone oil

Characteristics	Value
Specific gravity (30 ^o C)	0.923
Refractive Index (30 ^o C)	1.463
Acid value	3.36
Saponification value	192
Iodine value	123.3

Table 2—Fatty acid composition of argemone oil

Fatty acid	Per cent
Palmitic	12.6
Stearic	trace
Oleic	26.7
Linoleic	60.7

Table 3 —Physical properties of CWSA

Characteristics	Value
Colour (Gardner)	9
Viscosity (50 per cent solution in water at 30 c by F.C.B.IV Seconds)	78
Percentage solids	50.5
Solubility in water	Soluble in all proportions after neutralization with triethyl amine
Acid value (mg KOH/g)	69.2

under constant agitation for about 3 h. The reaction mass was cooled below 50^o C and product was washed with water to remove free maleic anhydride. Five sets of malenized oil were prepared as per composition (Table 5).

Neutralization of Malenized Oil with Triethyl Amine

The malenized oil was neutralized with calculated quantity of triethyl amine to get solubility. The amount

Table 4 — Physical properties of HMMM resin

Characteristics	Value
Colour (Gardner)	1
Percentage solids	99.7
Percentage free formaldehyde	0.15
Specific gravity (30 ^o C)	0.98
Viscosity at 30 ^o C by (Brook-field RVT with spindle 3 at 20 rpm)	21 Poise

required for complete neutralization was calculated on equivalent basis. (Table5) The neutralized mass was diluted to 50 per cent solids by using 10 per cent of Iso-propyl alcohol (co-solvent) and 40 per cent water.

Preparation of Stoving Compositions

The 50 per cent diluted solution of neutralized malenized oil was blended with water soluble HMMM resin in three proportions of 65:35, 50:50 and 35:65 on weight basis and the resulting compositions were diluted to 40 per cent solids and applied on test panels. Similarly stoving composition was also made from CWSA with CWSA:HMMM ratio 65:35 (conventional curing agent ratio) and applied on test panels. The coated panels were stoved at 120^o C for 30 min for complete curing of the films.

Chatacterization of the Coatings

The coatings were tested for general properties like per cent nonvolatile, viscosity, specific gravity, colour and drying and curing characteristics as per BIS methods¹⁴.

The coatings were also characterized by determining their IR spectrum. The representative IR spectrum of malenized argemone oil and HMMM cured film are given in Figure 3 and 4.

The cured films were evaluated for properties like adhesion and flexibility, scratch hardness, impact strength, and resistance to chemicals, water, and solvent.

Results and Discussion

The physico-chemical characteristics of argemone oil and physical characteristics of malenized argemone

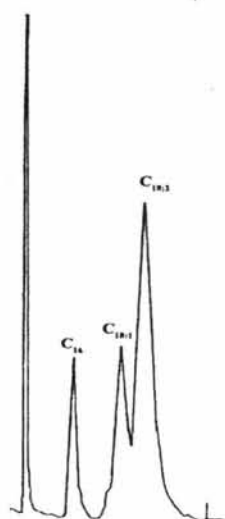


Figure 2— Gas liquid chromatogram of argemone oil

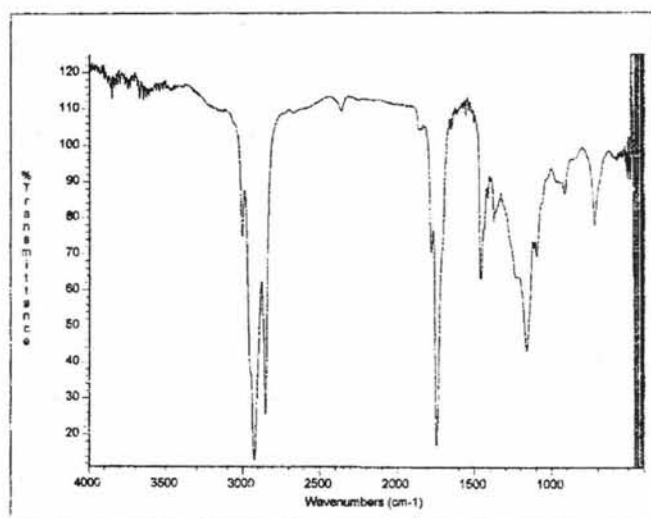


Figure 3—IR spectra of malenized oil

Table 5— Composition and chemical characteristics of malenized argemone oil

Composition code	Mole ratio of argemone oil: maleic anhydride	Per cent* free (unreacted) maleic anhydride	Predetermined	Acid value (mg KOH/g) Experimental	Amount(g) of agent (TEA) required for 100 g of malenized oil
Set I	1.0 : 1.0	4.5	109.2	99.50	17.91
Set II	1.25 : 1.0	4.1	89.1	82.10	14.78
Set III	1.5 : 1.0	3.8	75.1	68.5	12.33
Set IV	2.0 : 1.0	2.5	57.0	50.0	9.01
Set V	3.0 : 1.0	2.5	38.8	31.2	5.61

* On the basis of maleic anhydride taken for reaction

oil-HMMM based stoving compositions are shown in Table 6 and Table 7, respectively. Properties of the experimental stoving compositions, shown in Table 6, emphasize on the following significant details.

Mechanical Properties

Scratch hardness is found to be better in the case of compositions with higher HMMM ratio for all the experimental sets. This is due to more cross-link density¹⁵ and better integrity of the film. The CWSA based coat-

Flexibility and impact resistance are better for compositions with higher oil content, while those with higher HMMM ratio are unsatisfactory in this respect. This could be due to the plasticizing effect of oil in the film. The CWSA based coating, exhibited good flexibility and impact resistance.

Adhesion is also related with flexibility and film integrity. The compositions with higher oil ratio show better adhesion as compared to those with lower ratio but the overall performance is better for those with oil : HMMM

Table 6— Physical properties of malenized argemone oil – HMMM based stoving compositions

Set No.	Ratio oil : HMMM	Per cent NVM (120 ⁰ C / 2 h)	Viscosity by FCB IV at 30 ⁰ C	Colour (Gardner)	Sp.gravity at 30 ⁰ C
I	65 : 35	41.10	195 Sec	14	1.02
	50 : 50	40.50	187 Sec	12	1.04
	35 : 65	39.30	165 Sec	10	1.05
II	65 : 35	40.20	182 Sec	15	1.01
	50 : 50	41.05	172 Sec	11	1.03
	35 : 65	39.70	156 Sec	10	1.04
III	65 : 35	40.71	185 Sec	14	1.00
	50 : 50	41.08	175 Sec	12	1.02
	35 : 65	40.06	150 Sec	9	1.04
IV	65 : 35	41.70	179 Sec	12	1.01
	50 : 50	41.02	167 Sec	9	1.03
	35 : 65	40.50	152 Sec	7	1.05
V	65 : 35	39.82	165 Sec	10	1.02
	50 : 50	40.65	154 Sec	8	1.04
	35 : 65	39.95	148 Sec	6	1.05
VI	39 : 95	41.2	215 Sec	7	1.05

Chemical Resistance

Alkali resistance is inferior in the low oil containing compositions due to less cross-link density resulting in a permeable film, while compositions with oil : HMMM ratio 50 : 50 and 35 : 65 for Sets I to V show good alkali resistance due to higher crosslinking.

Like-wise, acid resistance of these two compositions for Sets I to V is reasonably satisfactory. Set II and III are superior to Set I compositions in overall properties of chemical resistance. This may be due to higher acid value of Set I compositions than those of Set II and III. The CWSA based coating shows good alkali and acid resistance.

Solvent and Water Resistance

Set III and IV with higher HMMM show better solvent resistance due to better film curing. The curing of malenized oil by HMMM is also supported by the results obtained from IR spectra. Water resistance is found to be better with 50 : 50 oil HMMM ratio. Set III and IV show better performance as compared to Set I and II due to less acidity which makes them less polar and less prone to attack by water molecules. The CWSA based coating

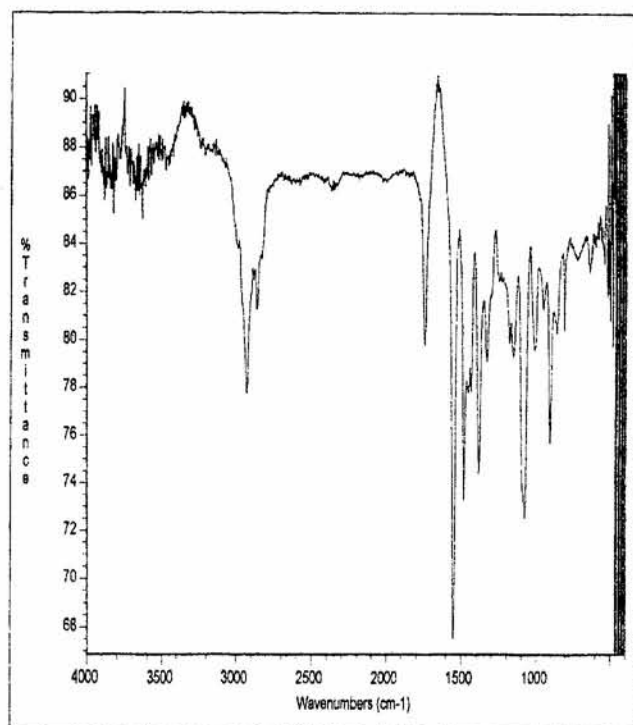


Figure 4— IR spectra of HMMM cured film

Table 7 – Stoved film properties of the stoving compositions

Set No.	Ratio Oil:HMMM	Scratch hardness kg (passes)	Impact resistance Lb.In. (passes)	Flexibility 1/8" mendral	Adhesion crosshatch	Chemical resistance unaffected			
						NaOH (3per cent) 2 h	HCl 5per cent 24 h	Xylene 72 h	Distilled water 48 h
I	65 : 35	0.900	150	P	F	0	1	1	1
	50 : 50	1.500	110	P	P	1	2	2	2
	35 : 65	2.10	60	F	P	3	3	3	2
II	65 : 35	1.0	150	P	F	0	1	1	1
	50 : 50	1.8	110	P	P	2	3	2	2
	35 : 65	2.3	70	F	P	3	4	3	3
III	65 : 35	1.10	170	P	F	0	1	1	1
	50 : 50	1.70	120	P	P	2	3	3	3
	35 : 65	2.2	90	F	F	4	4	4	4
IV	65 : 35	0.90	180	P	F	0	1	1	1
	50 : 50	1.70	100	P	P	2	3	3	3
	35 : 65	2.00	60	F	F	3	4	4	3
V	65 : 35	0.80	160	P	F	0	1	0	1
	50 : 50	1.50	100	P	P	2	3	1	2
	35 : 65	2.1	60	F	F	2	3	3	3

VI CWSA 2.5 110 P P 5 4 3 4

P = Passes the test,
 0 = Film completely removed,
 2 = Film partially cracked,
 4 = Slight loss in gloss,

F = Fails
 1 = Film cracked and partially removed,
 3 = Loss in gloss,
 5 = Unaffected

shows very good water and solvent resistance.

IR Spectrum

The IR spectrum (Figure 3) of malenized Argemone oil shows bands at 1743cm^{-1} attributed to ester stretching vibrations. Bands at 2858cm^{-1} and 2939cm^{-1} are attributed to (C – H stretching) alkane. Band at 1775cm^{-1} is due to anhydride stretching vibrations, which confirms the anhydride ring structure in the malenized oil. The IR spectrum (Figure 4) of the cured film based on malenized argemone oil and HMMM shows characteristic band at 1340cm^{-1} and 1407cm^{-1} for the aryl nitrogen stretching due to the presence of HMMM. The band at 1561cm^{-1} shows the presence of secondary amides, resulting from the reaction between HMMM and malenized argemone oil, supporting the curing of

Conclusion

It is concluded that the stoving composition with oil:HMMM ratio 50:50 exhibits better overall properties. The performance of these coatings for some of the experimental sets is very similar to that of the conventional water based alkyd coatings and therefore can be recommended for use in industrial finishes where good mechanical properties with mild chemical resistance are required.

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