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LEAD FREE EMULSION PAINT BASED ON SHORT OIL ALKYD

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Abstract:

Alkyd emulsion paste with low acid value and high % solid (50%) were to be prepared. These alkyd emulsion pastes have been used in formulation of synthetic emulsion paint. The proportion of emulsion paste binder is 15 to 30 % to get the desirable characteristics of paints. The emulsion paints is compared against commercial paint for the view point of technical and economical viability.

Normally we are required to add 1% of cobalt and 2 % lead as drier in many compositions. As we are thinking of lead free paint this small amount of drier should be avoided in final paint. In present formulation, we do not use any drier for any lead composition yet we are getting excellent drying and hardness property.

Keywords: *Short oil alkyd, Novel resin, synthetic emulsion paint*

1.INTRODUCTION

The surface coating industry is always in search of a water thinnable coating medium, which will have excellent hardness adhesion and resistance characteristics. Our institute is working on paint binder based on castor oil. We have developed several paint binders such as Castro alkyds and sorbo alkyds. At presents the acrylic binder are fast replacing oil base binders. The main disadvantage of oil binder is a sluggish drying property. Normally the surface dry time of many commercial acrylic paint is 10 to 15minutes while the alkyd based paints require 1 to 2 hour for surface drying.

2. EPERIMENTAL DETAILS

a)

Materials

A short oil alkyd resin[1] were prepared, raw material required, grade of material, source of material and specification have been given in table no.1. Alkyd resins were investigated in this research work by selecting soybean oil, glycerol, phthalic anhydride, maleic anhydride, rosin and benzoic acid.

b) Synthesis of Novel short oil alkyd Resin[7]

Compositions selected for the preparation of alkyd resins are given in table No. 2. The percentage of soybean oil was taken 13.86.The chain stopper compound like Benzoic acid and rosin was used in this formulation. The content of maleic anhydride varied between 1 to 4 % while phthalic anhydride varied between 30 to 40 %.

A) The Reactor :

The preparation of alkyd resin was carried out in a glass reactor[5]. The reactor consists of two parts. Lower part of the rector is a round bottom vessel with very wide mouth. The capacity of the flask is about 2 litres. The upper part of the reactor is its lid, having four necks with standard joints.

A motor driven stirrer was inserted in the reactor through the central neck, while another neck was used for thermometer. A condenser was fitted with the reactor through the third neck. And the fourth neck was used for dropping the chemicals in to the reactor. The reactor was heated by a electric heating mantle having special arrangement for smooth control of the temperature of the reactor. The speed of the stirrer was controlled by a regulator. The reaction vessel and its lid were tied together with the help of clamps. Alkyd resin were prepared using reactor. The schedule cooking process is given in figure No.1. Resin was analyzed physio-chemically. The analysis is given in table no.4.Then using alkyd resin, emulsion paste were prepared. Following method was used for the preparation of the emulsion paste.

Procedure: A known amount of alkyd resin was taken in a reactor fitted with a high speed stirrer and having heating arrangement. The resin was heated to 80^{o}c and to this a required quantity of solvent was added to form a resin solution. 1% of ammonia liquor was added drop by drop. A known amount of polyvinyl alcohol solution (10%) was added simultaneously with the ammonia with constant stirring. After the addition ammonia and P.V.A., 40 to 50 % hot distilled water was added at temperature of 80 ^{o}c slowly with high speed stirring. At the end, the remaining additives such as pine oil, sodium penta chloro phenol and solvent iso propanol was added to the emulsion. The emulsion thus obtained was stirred for about one hour; before been taken out and stored in an air tight container.

Preparation of emulsion paint:

Emulsion paints were prepared from the emulsion paste.

Preparation:

i) Calculated amount of pigments, extender, emulsion paste and solvents were weighed and grinded in a ball mill for about 11-14 hours.
ii) The grinding process was continued till the required fineness of grind was obtained.
iii) At the end, calculated amount of solvent was added to adjust its consistency.
iv) The paint thus prepared was then transferred to an air tight container.
v) The paint was evaluated for physicochemical and film properties like viscosity, hiding power, scratch hardness, gloss and resistance to water, acid, alkali and solvent.

2.07 Methods of analysis:

(A) Physico-Chemical Properties:

(i) Acid Value:

Acid value of the samples were determined by ASTM standard Method, using following formula

$$A.V. = \frac{56.1 \times V \times N}{\frac{W \times m}{100}}$$

where,

V = Vol. of alcoholic KOH solution.

N = Normality of alcoholic KOH solution.

W = weight in gms. of alkyds resin solution taken

M = % of solid in the resin solution.

(ii) Iodine value:

$$\text{Iodine value} = \frac{12.69\ (B - S) \times N}{W}$$

Where;

W = Weight of the sample in grams.

N = Normality of sodium thiosulphate solution

B = Volume in ml of thiosulphate solution used in Blank

S = ml of thiosulphate solution used for sample

(iii) **Saponfication Value:**

$$\text{Saponification value} = \frac{56.1 \times (B - S) \times N}{\text{Weight of the sample}}$$

(iv) Specific Gravity:

Specific gravity of alkyd resin samples were determined by using a cylindrical cup of 100 cubic centimeters volume, furnished with a close fitting lid pierced with a small hole. It is used in a similar manner to a specific bottle.

(v) Volatile content:

It was determined by weighing out 2 to 3 gms. of alkyds resin sample in to a petridish and heating for about 3 hours in an oven at 105 ^{o}c. It was cooled weighed and reheated for a further half-hour to check that the weight was constant. The volatile content is expressed as a percentage of the original resin.

(vi) Solid content:

The percentage of solid in the alkyd resin was calculated as follows

% solid = (100 - volatile content)

(vii) Viscosity :

Viscosity of alkyd resin sample was determined by ford cup method. Ford Cup consists of a cylindrical metal cup with parallel side and a conical base.

The time required for the cup to get empty through the orifice was noted and result was expressed in seconds.

(viii) Film properties

Film of samples were evaluated for their drying time, gloss, scratch hardness, resistance to water, chemicals and solvents using following methods.

(i) Preparation of metal panels:

Mild steel panels (16 cms x 5 cms) were first freed from surface imperfections such as rolling marks, scores etc. They were then immersed in kerosene and abraded with emery paper and dusted off. The panels were finally degreased by swabbing with sulfur free toulene, followed by methanol and then dried prior to painting.

(ii) Application of thin film:

A thin film of the sample was applied on the metal panel by brush, taking care that all the coatings were of approximately same thickness and uniform without any brush mark. About 10 panels were prepared for each sample.

(iii) Drying time (Air drying):

The set of coated panels were placed horizontally on the table for air drying and times required to surface dry and dry, were recorded.

(a) Surface dry: it means point has been achieved if the finger will not pick up material when touched lightly to the surface.
(b) Hard dry: it is the point at which considerable pressure and rotating motion of the finger does not distort the film.

(iv) Determination of Gloss:

Gloss is the ability of a surface to reflect light regularly. It may be defined as the degree of approach to a smooth plane mirror surface. More the microscopic roughness, the lower is the gloss.

Gloss is measured by an instrument known as gloss meter (The AIMIL gloss/ reflectance meter). It measures specular reflection of 45^{o} of angle of incidence. The specularly reflected light is measured with the help of a suitable galvanometer calibrated to give directly the gloss from zero (for a matt or flat surface) to 100 (for a full gloss surface like plane mirror).

The photocell was checked for zero gloss value. The instrument was calibrated with low and high gloss standards with the help of sensitivity control. Then the photocell head was placed on the dried film of a resin under test and several readings of the galvanometer were taken by placing the gloss meter head at various different places on the same panel. Mean of the different values was taken as the gloss value.

(v) Scratch hardness:

In this test, resistance to scratching under a specified load, of a dried film of the resin is tested.

The metal panel was locked on the sliding panel of the apparatus. The needle (made of hard steel is hemispherical and 1 mm in diameter) was fixed at the end of the counter poise, which was kept horizontal by adjusting the length of the needle. The panel was then drawn under the needle slowly (the rate of 30-40 mm/second) The weight on the counter poised arm, which produced a scratch showing bare surface was noted.

(vi) Hiding Power :

A plain plate was placed over a black and white chart in which there were adjacent black and white

squares. Paint was applied over the glass plate with the help of a fine brush, from a previously weighed paint container. The weight was taken along with the brush. Sufficient paint was applied in glass plate to cover the known area, so that the black and white blocks were just invisible. The weight of the paint container with brush was taken again. Difference between two weights was the quantity of paint applied.

(C) Resistance to water and chemicals:

Metal panels with well dried coated films were immersed separately one each in distilled water, 30% salt water, 2% Detergents solution, 3% H_2SO_4, 3% HNO_3 at room temperature for 48 hours and in 3 % NaOH solution for 15 minutes. They were then renoved and examined whether films were disintegrated, blushed or swelled. Whether the films were unaffected, slightly affected with loss of gloss or affected badly or films were removed. The resistance of the films was termed as very poor, poor, good or excellent depending upon the condition of the films as follows.

Excellent = No effect on the film.
Good = Film affected slightly with loss of some gloss slowly
Poor = Film affected badly but remains intact.
Very poor = Film removed completely.

(D) Resistance to solvents:

Metal panels with dried films were immersed separately one each in acetone, alcohol, xylene and turpentine for 10 minutes. They were then removed and examined. The resistance of the films were reported as excellent, good, poor or very poor depending upon the condition of the films.

The enamel paint prepared was analyzed for physicochemical and film properties. These properties are given in table no. 5 and 6. Its resistance to water, acid, alkali, detergent and solvent have been given in Table No.7.

RESULT AND DISCUSSION

In general, the reported compositions of short oil alkyds have an oil percentage of 25 to 35. If we try to reduce the content oil below this level the control of reaction is lost and there is heavy tendency of gelation of alkyd formulation. If we make use of chain stoppers like Benzoic acid or Rosin, perhaps the proper control of the reaction can be achieved.

Table 2 gives the composition of short oil alkyd using soybean oil. Here soybean oil is specifically chosen because it does not contain higher proportion of linolenic acid. So tendency of gelation can be reduced to some extent by using soybean oil. Rosin is having bulky structure with molecular weight of 300. This is bulkier molecule therefore it will arrest and regulate the growth of polymer. About 5% of Benzoic acid is known to control and to regulate the fast polymerization reaction. There are several distinct advantages in this reaction. First of all, the total time of heating is very less. It is just about 4 to 5 hours. Normally a standard alkyd cook required 12 to 16 hours for cooking therefore there is definite saving of time and energy. Highest temperature required in this process is 220^{o}c. normally while making use of D.C.O. in alkyd we have to cross the temperature of 270 ^{o}c. The energy required, fuel cost, color and quality of resin demand that the highest temperature should not go above 220^{o}c.

The analysis of this short oil alkyd is given in table 3. The viscosity of composition is quite high. Drying time is quite satisfactory. The surface dry time is only 15 minutes, which is remarkable property of this composition. Different compositions of Synthetic enamel paint were prepared based on this alkyd using TiO_2, ZnO as a pigment. The physico-chemical properties are studied in table 6. The sample has high hiding power. The viscosity is quite satisfactory for application by spray or brush. The hiding power of paint is excellent i.e.14 to 15 square meter per liter. The adhesion of paint sample is also excellent. The surface dry time is very less it is just 15 minutes while hard dry time is 6 hours. Scratch hardness of the paint sample is above 1000 grams. The resistance to water, 3% sulphuric acid for 48 hours is excellent while resistance to all detergent and 3 % sodium hydroxide is poor. Finally, the resistance of paint sample for all the solvents is excellent. Analysis, film properties and its resistance power is given in table no.7,8,9.

In general, the resistance of paint samples to solvents, 3% detergent, 3% alkali and water is excellent. Resistance in water is good even after 7 days. The only defective part is poor resistance for 3% H_2SO_4.

CONCULSION

The following conclusion stand confirmed in the light form of the above experimental work.

1) Normally, short oil alkyd contains 25 to 35% oil in the final composition. Here we have made an attempt to prepare alkyd with very low oil length. The oil has been kept very low (13.85 %). Normally sample gel at such a lower percentage of oil. However by making using of chain stoppers we control reaction in workable range.
2) Thus the chain stoppers like benzoic acid and rosin is used to control reaction. Phthalic anhydride is used as major acid ingredient. The polyol used is glycerol.
3) The major advantage is saving of time in cooking of batch. Conventionally the alkyd batch required cooking schedule of 12 to 16 hours. While here the complete schedule is of 8 hours. Thus using this composition we can increase the capacity of the plant. Thus overall efficiency of process can be improved.
4) In D.C.O. resonated alkyd for dehydration stage we have to increase temperature 275 ^oC. Thus higher temperature in the range of 270 to 280^{o}c is required. Here in present work, the highest temperature required is 220 ^{o}c. Usually we work in lower temperature of 180 to 190 ^{o}c. From the viewpoint of controlling reaction, the lower cooking temperature is attractive feature. The energy consumption is also reduced. Looking to the skyrocketing prices of fuel and electricity, a lower temperature is certainly advisable and profitable.
5) Useful emulsion paste base on alkyd has been prepared.The composition of emulsion paste is given in table no4. In the composition emulsion paste distilled water to the extent of 33 to 56 % can be incorporated. The solvent used in paste is smaller quantity of iso propanol, pine oil and moderate quantity of xylene and butanol. A small amount ammonia have been incorporated for the residual acidity of alkyd. A small quantity of P.V.A. 1 to 3 % has been incorporated to improve the homogeneity, adhesion and other film properties of paints. A small quantity of commercial homogeniser 1 to 2 % has been used in emulsion paste. This paste

has low acid value and contains 40 to 50 % non-volatile. The paste has stability of more than three month. A small quantity of sodium penta chlro phenol has been incorporated to improve stability. In general, excellent paint composition can be prepared by using 20 to 60 % paste.

6) The paint compositions have excellent physico-chemical properties. The fineness of grind, specific gravity, hiding and viscosity is comparable to commercial sample. Composition is totally lead free hence reduces water contamination.
7) Resistance of film to water even for 7 days is excellent. Many formulations have excellent resistance to detergent and solvent. Acid and alkali resistance needs improvement.
8) Most important and attractive feature of this work is thinning paint with organic solvent as well as water. Thus addition of 10 % of organic and 10% of water will not adversely affect consistency of paint.
9) Pilot Plant trials and commercial marketing of these products should be undertaken to prove these experimental results.

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TABLE 1: SOURCE AND ANALYSIS OF RAW MATERIAL/ CHEMICALS.

Raw materals/ chemicals/ reagents	Grade of the Materials	Source of The Materials	Results of Analysis
Soybean oil	Commercial grade	Swastik Acids and Chemicals Nagpur	Acid value = 3 Sap. Value =190 Iodine value = 130 Sp. gravity = 0.923
Rosin	-do-	-do-	Acid value = 166.5
Glcyerol	Lab. Chemicals	E. Merch (India) Ltd. Mumbai.	% purity = 98 density =1.255 moisture content = 1.2 %sulfated ash = 0.005
Maleic anhydride	Lab. Chemicals	Swastik Acids and Chemicals Nagpur	Acid value = 1130.0

Phthalic anhydride	Lab. Chemicals	Swastik Acids and Chemicals Nagpur	Acid value = 750.0
Benzoic acid	Lab. Chemicals	Samar Chemicals, Nagpur	% purity = 99 m.p. = 121 ^{o}c
Titanium dioxide	Anatase grade	Travancore titanium products Ltd., India	Oil absorption= 21.8%
Zinc oxide	Lab. Chem.	E. Merch. (India) Ltd. Mumbai	Oil absorption =15.9%
Xylene	Lab. Chem	Loba Chemie Pvt. Ltd. Mumbai	B.P. = 138^{o}c Sp.gr = 0.859
Turpentine	Commercial grade	Swastik Acids and chem. Nagpur	B.P. =158.5^{o}c Sp.gr. = 0.872
Butanol	Lab. Chem	S. Define chem. Ltd. Boisar.	B.P. =116.5oc Sp.gr. = 0.810

TABLE 2: COMPOSITION OF SHORT OIL ALKYD BASED ON SOYBEAN OIL AND PHTHALIC ANHYDRIDE

Ingredient	**Composition % by weight**
Soybean oil	13.86
Glycerol	25.27
Phthalic anhydride	36.90
Maleic anhydride	2.76
Benzoic acid	2.76
Rosin	18.46

Figure No.1

HEATING SCHEDULE FOR SHORT OIL ALKYD

Mix well all ingredient except ph. Anhydride + 5 % XBT solvents

↓ Heat to about 130 ^{o}c

Add ph. Anhydride

↓ Heat to 220 $_{o}$c

Maintain for 1 hour

↓ Cool to 210 °c

Maintain for 1 hour

↓ Cool to 200 °c

Maintain for 2 hour 30 minutes

TABLE 3: ANALYSIS OF SHORT OIL ALKYD .

Acid value	36.7
% non volatile	90.2
Viscosity of 43 % solid using Ford cup no.4 at 30 °c in seconds.	40
Drying time Surface dry (in minutes) Hard dry (in hours)	 15 5

TABLE 4: COMPOSITION OF EMULSION PASTE BASED ON SHORT OIL ALKYD

Ingredient	**Composition % by weight**
Short oil alkyd	40.6
Ammonia	0.81
P.V.A.	0.81
Distilled water	27.61
Pine oil	0.81
S.P.C.P.	3.0
Iso. propanol	2.0
Solvent (xylene: butanol)	24.26

TABLE 5: ANALYSIS OF EMULSION PASTE BASED ON SHORT OIL ALKYD

Acid value	11
% Non volatile	49
Viscosity by Ford cup no.4 at 30^{o}c in minutes.	5

TABLE 6: COMPOSITION OF EMULSION PAINTS BASED ON EMULSION PASTE OF SHORT OIL ALKYD.

Ingredient	**Composition % by weight**			
	EP1	**EP2**	**EP3**	**EP4**
TiO2	13.84	6.5	4.97	3.78
ZnO	2.76	1.08	0.90	0.81
Ph. Green	0.29	0.15	0.09	0.08
Alkyd	14.36	27.86	29.86	33.8
Ammonia	0.28	0.23	0.19	0.15
p.v.a.	0.28	0.23	0.19	0.15
Distilled water	9.73	8.62	6.61	5.22
Pine oil	0.28	0.23	0.19	0.15
S.P.C.P.	0.28	0.23	0.19	0.15
Iso propanol	1.41	1.10	0.98	0.95
Solvent	56.57	53.80	55.57	54.86

TABLE 7: PHYSICO-CHEMICAL ANALYSIS OF EMULSION PAINTS BASED ON EMULSION PASTE E2.

Characteristics	**EP1**	**EP2**	**EP3**	**EP4**
Fineness of grind in micron	2	2	2	2
Specific gravity	1.10	1.09	1.05	1.02
Viscosity by Ford cup no.4 at 30^{o}c in seconds	80	80	80	80
Hiding power in sq. meter per liter	13.02	8.1	7.2	6.5

TABLE 8: FILM PROPERTIES OF EMULSION PAINTS BASED ON EMULSION PASTE E2.

Characteristics	**EP1**	**EP2**	**EP3**	**EP4**
Drying time Surface dry in seconds Hard dry in hours	 10 4	 15 6	 15 8	 20 8
Scratch hardness in grams	1000	1000	1000	1000
Adhesion	Excellent	Excellent	Excellent	Excellent
Gloss	Matt	Matt	Semi gloss	Semi gloss

TABLE 9: ANALYSIS OF EMULSION PAINTS RESISTANCE TO WATER, ACID, ALKALI, DETERGENT AND SOLVANT.

Solution	**EP1**	**EP2**	**EP3**	**EP4**
Water				

48 hours 7 days	Excellent Good	Excellent Excellent	Excellent Excellent	Excellent Excellent
Acid 3%H2SO4 48 hour	Poor	Poor	Poor	Poor
Alkali 3%NaOH 15minutes	Excellent	Excellent	Excellent	Excellent
3% Detergent 48 hours	Excellent	Excellent	Excellent	Excellent
Solvents (15min.) Xylene Butanol Turpentine	 Excellent Excellent Excellent	 Excellent Excellent Excellent	 Excellent Excellent Excellent	 Excellent Excellent Excellent

Excellent = Film unaffected Good = Film slightly affected

Poor = Film affected Very poor = Film completely removed