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Synthesis of Enamel Paint based on Novel Rosinated Maleinized Castor Oil using Zinc Oxide as a Natural Drier

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Abstract: Now a day there is a global trend of replacing petroleum based products with renewable sources like plant extracts, Rosin, natural dryers in commercial products such as Paints, Varnishes, etc. The petroleum products are sourcing in price and availability, we have to search for alternatives particularly from vegetable sources. Being of natural origin, these derivatives are expected to be fairly biodegradable. Malenized vegetable oils have been used in various industrial products like wall finishes, water thinnable paints, electrodeposition paints, water thinnable primers and printing inks. The main aim of the project is synthesis of Zinc Oxide based natural drier as a novel alternative for high cost conventional driers using Rosinated Malenized Castor oil (RMCO). In the present work, enamel paint based on castor oil & Maleic anhydride has been prepared, and its suitability for results has been verified. Then the Malenized castor oil is further modified with Rosin for increasing its usability. The reaction conditions have been standardized to get with desired acid value, and degree polymerization. Synthetic driers are the costly ingredient in paint and presence of metal like lead, cobalt causes pollution and environmental harms. We have aimed to develop the paint composition which will dry without use of synthetic drier and to prepare eco-friendly composition with ZnO as natural drier. During synthesis we have studied the different physical properties of paint for different ZnO content in formulation. The paint based on ZnO and Rosinated Maleinized Castor Oil is biodegradable and ecofriendly, which is the need of the hour.
Key Words: Rosinated Malenized Castor Oil (RMCO), Maleic Anhydride, Maleinized Oil, Enamel Paints, ZInc Oxide .

INTRODUCTION:

India is one of the leaders in castor oil production. We have selected Castor oil as base for product preparation. As India is one of the leaders in castor oil production, it is beneficial for us to have much availability of castor oil as a raw material. India exports castor oil to other countries. The major consumer countries of castor oil with their annual consumption figures in Metric Tones (2008-2009)[1]

Table A-consumoption of castor oil

Country	Consumption
European Union	130000
India	85000
China	170000
Brazil	60000
USA	40000
Japan	20000
Thailand	15000
Others	10000

GROWTH IN THE CASTOR OIL BASED INDUSTRY:

Table B-Growth of castor oil based industry

Sr.No	Industry	% Growth Based on 2009 Data	Potential (Metric Tones)
1	Lubricants and Greases	2	44Metric Tones by 2012
2	Coatings	4.9	(11% in Asia)
3	Personal care and detergent	6	$375 billion by 2012
4	Surfactants	4	$16.65 billion by 2012
5	Oleochemicals	4	$ 8.5 billion by 2012

Today is the world of Colour and Contrast. In such an environment, decoration and appearance or painted surface is as important as its durability. Anticorrosive paint reserves various aspects from corrosion, while the silky matt finish emulsion paint and enamels enhances the beauty of wall, house and enlightening surroundings. The paint field is advancing very rapidly. The application is of versatile nature and also the need to apply the paint increases, depending on the substrate, environmental conditions etc. Paint is a mechanical dispersion of pigment into resin with additives and solvent. Paint is applied for decoration and protection. The decorative paints are mostly based on water whereas the protective paints are solvent based. Each ingredient has its own contribution[2,3]. The resin covers the pigment particles and helps to build the film. It gives number of important properties-gloss, adhesion, flexibility, hardness, weather resistance and chemical resistance properties. Whereas pigments gives color, U.V resistance, light resistance, etc. Solvent is added only to reduce the viscosity for application.. Additives are for enhancing the properties of paint including drying, antisetteling, antiskining, wetting and dispersing agents etc.

ROSIN ADDITION

The rosin is a natural resin obtained from pine tree. Gum rosin, wood rosin and turpen oil rosin are the types of rosin. It contains about 90% Abietic acid and its isomers- dextropimaric and levopimaric[5].

Rosin maleic adduct

Malenization: Addition of maleic anhydride

Rosin Acids having conjugated pair of double bonds form Diels Alder addition product with maleic anhydride. A Diels–alder type of addition is possible with Levopimaric acid but not with abietic acid, as abietic acid has no conjugated double bonds in the ring. However, when the temperature is raised, abietic acid isomerizes to Levopimaric and the (1:4) addition reaction take place. The adduct have higher softening points and greater acidity because of their increased functionality. They find use as polybasic acids in the preparation of alkyd resins, oleo resinous vehicles and hard resins. Frequently the adduct is used as the ester and prepared by reaction of glycerol or pentaerythritol with rosin and maleic anhydride. This is an example of many instances in which both functionalities, the carboxyl group and the double bonds, must be altered to obtain modified rosin with the desired characteristics. These esters are used extensively in protective coatings and printing ink formulations. Maleic modified rosin esters contribute the properties of hardness high luster and adhesion[6,7]

Physical Properties of Rosin:

Softening Point ^{0}C	**70-75^{0}C**
Acid Value	160
Sap Value	165
Iodine Value	200
Unsaponifiable Material%	6
Ash %	0.05
Specific Gravity at 20^{0}C	1.089
Refractive index at 20^{0}C	1.541
% Insoluble	0.1 to 1.0
% Volatile Matter (max)	2.0

The addition of rosin results in

- Increase in complexity of drying oil and hence polymerization with increase in molecular weight.
- Increase in Gloss and hardness of product.

Zinc Oxide is a synthetic based pigment that inhibits mold growth, if present in high levels (about 30% by weight). The basic nature of zinc oxide leads to interaction with paints of high acid value with the formulation of zinc soaps. These can mechanically reinforce the film but can cause embrittlement on exterior exposure. Zinc oxide is a very effective wetting and pigment-dispersing agent[8]. Zinc oxide also helps to promote hardness, gloss and color retention. Because of its pale color, relatively large amounts can be added without discoloring the paint film.

EXPERIMENTAL WORK[10,11]:

Synthesis of Maleinized Oil:

1) The Reactor: The preparation of maleinized oil was carried out in a glass reactor. The reactor consists of two parts. Lower part of the reactor is a round bottom vessel with very wide mouth. The capacity of the flask is about 2 liters. The upper part of the reactor is its lid, having four necks with standard joints. A motor driver 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 into the reactor. The reactor was heated by an electric heating mantle having special arrangement for smooth control of the temperature of the reactor. A regulator controlled the speed of the stirrer. The reaction vessel and its lid were tied together with the help of clamps[9].

2) Analysis of Castor Oil: Castor Oil is the main ingredient to be used in manufacturing maleinized oil, was analyzed for its properties such as Acid value, Iodine value, Saponification value, etc. which are described in table.

3) Compositions: Maleinized oil from various compositions of Castor Oil and maleic anhydride were prepared by batch process. These compositions are given in table.

4) Methodology and cooking schedule of maleinized oil synthesis: The reaction, temperature and addition of ingredients are detailed below;

Step1) Maleic Anhydride, Sodium bisulphite and sodium bisulphate were added in approximately quantity of Castor Oil to form a slurry, by heating it on hot plate at a temperature of about 120°C.

Step2) The remaining amount of oil was then introduced in the rector and heated with agitation to a temperature of 100°C in one hour.

Step3) The slurry prepared above in step1 was added slowly at this stage in about 30 min with gradual increase in heating to a temperature of 225°C.

Step4) The whole reaction mass was held at temperature of 225°C for 1 hour and then the temperature was slowly brought down to 220°C, 210°C, 200°C, 180°C, 150°C in next 5 hrs of heating.

Step5) the darkening and thickening (I.e. viscosity) of treated oil was observed periodically and the reaction was terminated when sufficient viscous mass was observed giving an indication of almost complete reaction of maleic with oil.

Batch was withdrawn and filtered; to remove unreacted or charred maleic, in a tin container and weighed to find out % yield.

Table no.1 Analysis of Castor Oil

Sr. No.	**Property**	**Value**
1	Acid Value	2.0 max
2	Iodine Value	82
3	Saponification Value	177
4	Hydroxyl Value	160 Min.
5	Refractive Index	1.477
6	Density(In gm/cc)	0.952
7	Color	Pale dark yellow
8	Consistency	Thick

Table No. 2 Composition of Malenized Castor Oil

Ingredients	**% by weight**
Castor Oil	83.5
Maleic Anhydride	15
Sodium Bisulphate	1
Sodium Bisulphite	0.5

Table No. 3 Cooking schedule for Maleinized Oil synthesis

Time (Hrs)	Temperature (°C)
0	0
1	100
2	150
3	200
4	225
5	225
6	220
7	210
8	200
9	180
10	150

Table No. 4 Analysis of Maleinized Castor oil

Sr. No.	Property	Value
1	Acid Value	138.2
2	Iodine Value	35
3	Saponification Value	297
4	Refractive Index	1.4215
5	Consistency	Viscous
6	HLB Value	12.5
7	Color & Consistency	Dark Brown and Thick

Modification of Maleinized Castor Oil with Rosin[12]

- **Formulation and synthesis[15]**
- **Heating schedule**
- **Analysis of product and Rosinated Maleinized Castor Oil (RMCO) as such for drying.**

FORMULATION AND SYNTHESIS[13,14]

For the synthesis of R.M.C.O, a glass beaker, electric heater, stirrer and thermometer are required with Rosin as main ingredient to be added. The formulation and heating schedule is given below

FORMULATION

Table No. 5 Formulation of R.M.C.O

Sr.No.	Ingredient	% by weight
1	M.C.O	80
2	Rosin	20

HEATING SCHEDULE

Table No. 6

Sr.No.	Temperature (^oC)	Time (hr)
1	100	0.25
2	150	1.0
	Total	1.25

ANALYSIS OF ROSINATED MALEINIZED CASTOR OIL (R.M.C.O.)

Table No. 7 Properties of R.M.C.O

Sr. no	Properties	Value (%)
1.	Acid value	60.00
2.	Sap value	260.00
3.	% Solid	97.00
4.	Consistency	Viscous
5.	Specific Gravity	0.940
6.	Appearance	Clear

RAMCO AS SUCH FOR DRYING[16,17] :

- Checked the drying property of R.M.C.O, it is applied over the panels with the suitable solvent Turpentine and with brush. The panels (wood and tin) are allowed to dry at ambient conditions.
- After observing the panel for drying over a consecutive first, second and third day, it was not surface dry on the first two days but it showed surface dry on third day. Means the R.M.C.O works in paint as resin but it would require more days to thorough dry. So further modification was done with Rosin to prepare Rosinated and Malenized Castor oil (RAMCO).

Table No. 8 Formulation of Enamel

Sr.No.	Ingredients	% by weight
1	TiO_2	25
2	R.A.M.C.O (95.32%)	50
3	Soya	2
4	ZnO	5
5	Turpentine	18

FORMULATION WITH DIFFERENT PERCENTAGE OF ZINC OXIDE (ZNO) PIGMENT.
Table No. 9

Day	Sr.No.	Ingredients	% by weight	For 300grm batch	PBR
1	1	TiO_2	25	75	
	2	R.A.M.C.O	50	150	
	3	Soya	2	6	
	4	**ZnO**	**5**	**15**	0.6:1
	5	Turpentine	18		
2	1	TiO_2	25	75	
	2	R.A.M.C.O	50	150	
	3	Soya	2	6	
	4	**ZnO**	**10**	**30**	0.7:1
	5	Turpentine	22		
3	1	TiO_2	25	75	
	2	R.A.M.C.O	50	150	
	3	Soya	2	6	
	4	**ZnO**	**15**	**45**	0.8:1
	5	Turpentine	25		
4	1	TiO_2	25	75	
	2	R.A.M.C.O	50	150	
	3	Soya	2	6	
	4	**ZnO**	**20**	**60**	0.9:1
	5	Turpentine	29		

Analysis of Enamel Based on R.M.C.O
Table No. 10

Day	% ZnO	% Solid	Viscosity (Sec)	Density (kg/lit)	Grinding (Hg)	Hiding Power (m^2/lit)	Drying time
1	5	68.95	120	1.10	3+	12.25	Tack free- 1 days Surface dry-2days
2	10	69.00	120	1.12	3+	15.94	Tack free- 12 hrs Surface dry- 18hrs Hard dry-1.5 days
3	15	70.10	120	1.14	3+	15.99	Tack free- 7 hrs Surface dry - 12hrs Hard dry- 20hrs
4	20	71.62	120	1.16	3+	16.00	Tack free- 4.5 hrs Surface dry-9 hrs Hard dry- 12hrs

Comparison of Enamel based on R.M.C.O with Commercial Sample
Table No. 11

Paint	% ZnO	% Solid	Viscosity (Sec)	Density (kg/lit)	Grinding (Hg)	Hiding Power (m^2/lit)	Drying time
Commercial	10	66.00	120	1.10	5+	12.25	Tackfree-4hrs Surface dry- 6hrs Hard dry- 9hrs
Prepared	20	71.62	120	1.16	3+	16.00	Tack free- 4.5 hrs Surface dry-9 hrs Hard dry- 12hrs

RESULT AND DISCUSSION:

The analysis of available castor oil is given in Tables No-1. The analysis of prepared Malenized oil samples is given in Table No. 2. The cooking schedule and order of addition of various ingredients is also given in Table No. 3. Acid Value and Saponification Value indicates substantial induction of maleic anhydride in the oil molecules. These data of analysis of maleinized castor oil is shown in Table No-4. Modification of Maleinized Castor Oil with Rosin and its heating schedule is given in Table No. 5 and 6. Several compositions of paint system based on Rosinated Malenized Castor oil have been prepared. Various percentage of ZnO has been added to impart drying of paint film and the formulations are shown in Table No.9 The viscosity, hiding power, density of prepared paint system from Rosinated Malenized castor oil are given in Table No.10. The sample of Malenized oil chosen for the preparation of paint system which gives most excellent characteristics as alkyd resin and comparable properties with conventional paint system is shown in Table No- 11. During preparation of the enamel paint all the ingredients are mixed in proper ratio and grinded to proper dispersion for required grinding of gauge (Measured by Hegman Gauge). The viscosity is adjusted to application viscosity range (around 120 sec. by ford cup no.5) using solvent of natural origin turpentine. On the first day all the parameters are checked and the paint is kept for overnight after applying it to steel panel for checking drying characteristics. On the next day paint sample is checked for increase in viscosity. The viscosity increased is lowered down to application viscosity and all the parameters are gained checked, all this is carried out repeatedly till the desired drying characteristics is achieved. % Solid in the paint system is in the range of 65-68%. Scratch hardness and adhesion of all paint system samples is good. The surface dry time is about 9 Hrs while hard dry time is 12hrs. Scratch hardness of the paint system sample is about 1000 grams. The viscosity is quite satisfactory for application by spray or brush. The hiding power of paint is excellent i.e.11 to 15 square meters per liter. The adhesion of paint sample is also good.

CONCLUSION:

The following conclusions stand confirm from the above research work which is explained as follows-

1) Synthesis of Malenized oil has increased the usability of the vegetable origin oil to a very vast extent, the reason for this is,
   a) Reaction is simpler
   b) Modification requires lesser temperature compared to the alkyd formation from vegetable oils.
   c) Molecular weight of the vegetable oil increases to a very desirable range.

2) Rosination of Malenized castor oil is another useful finding in the research. This reaction is carried out using ingredients shown in table no. 5 and they are heated together to get desired properties as shown in table no.6 where rosin of natural origin is reacted with Malenized castor oil to yield a resin of high molecular weight which is used as a binder for enamel paint formulations.

3) The formulations of enamel paints are shown in table no. 9 and analysis is reported in table no. 10. From the results shown in both the tables it can be clearly distinguish that percent solid has comparatively increased and similar is the case with the hiding power. But one important noticeable point is the drying time, with increase in Zno percentage drying time is decreasing which is remarkable finding of this research.
4) All the samples prepared are comparable with the commercial samples as it can be seen from table no.11.

The novel findings of this research shows good implementation of chemistry of natural origin showing

novel formulations which has opened new horizons for two pack systems in the paint industry. Which not only fulfill the environmental problems caused by synthetic metal driers but also involves good use of vegetable origin products leading the research towards green chemistry.

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