DEHYDRATION OF CASTOR OIL OVER PAKISTANI BENTONITES

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Dehydration of castor oil has been attempted by passing the oil through a column packed with activated Pakistani bentonites as such or coated with various salts. The clay coated with $NaHSO_4$ gives the best results in terms of high iodine value and light colour of the product.
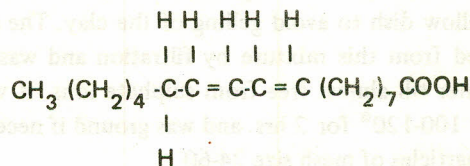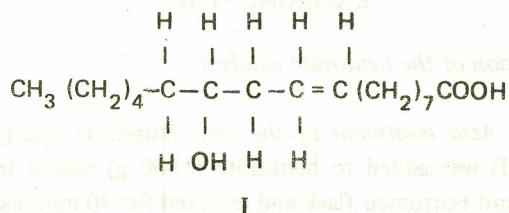
INTRODUCTION

Dehydrated castor oil was originally developed as a substitute for tung oil and unfortunately, even today, this idea still prevails to some extent [1]. It is nevertheless a unique drying oil and different from tung, linseed or oiticica oil. It can be considered as an intermediate between tung oil and linseed oil.

Dehydrated castor oil is a superior vehicle in paints due to its water absorption properties. It is also free from acetylenic fatty acids which cause the dark colouration of the coatings obtained using other oils. Therefore, it finds extensive use in the white or light coloured interior finishes where outstanding nonyellowing characteristics, good flexibility and excellent colour retention of the protective coatings is desired. However, dehydrated castor oil varnishes suffer from after-tack effects, which are due to the presence of the decomposition products or undehydrated castor oil or the oxidation products produced within the film during drying.

Alkyd resins [2] obtained from dehydrated castor oil are satisfactorily cured at room temperature. This property offers a wide application in film formation on machinery, metal containers, signs and for metal decorative purposes. It is also used as a plasticiser in conjunction with urea or melamine resins.
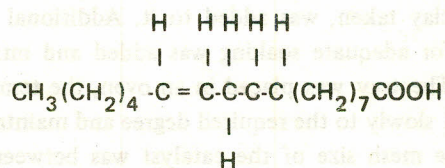
All these advantages render dehydrated castor oil suitable in great many products where no other oil serves the purpose. About 45% of the castor oil produced in the United States is used for its conversion to dehydrated castor oil, but in Pakistan it has not yet been properly introduced. Instead refined linseed oil which is largely imported, is used. No doubt the production [3] of castor seed oil in Pakistan is only 1.35% of the world production but it can be very easily increased in future through the production of dehydrated castor oil.

Chemically castor oil [4], like other fixed oils, has a glyceride structure of which about 80% of the acid component is ricinoleic acid. As a result of the dehydration of this oil, hydroxyl group of the ricinoleic acid (I) is eliminated and a double bond is introduced. This process may lead to the formation of either the conjugated isomer (II) or the non-conjugated isomer (III).

$$CH_3\,(CH_2)_4-\overset{\overset{\displaystyle H}{|}}{C}-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle OH}{|}}{C}}-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-\overset{\overset{\displaystyle H}{|}}{C}=\overset{\overset{\displaystyle H}{|}}{C}\,(CH_2)_7\,COOH$$

I

$$CH_3\,(CH_2)_4\text{-}C\text{-}C=C\text{-}C=C\,(CH_2)_7COOH$$

9, 11 - Linoleic acid

II

$$CH_3(CH_2)_4\text{-}C=C\text{-}C\text{-}C\text{-}C\,(CH_2)_7COOH$$

9, 12 - Linoleic acid

III

None of the dehydration processes yields a single isomer exclusively and the composition of mixture obtained depends upon the experimental conditions used. The desirable conjugated isomer [5] (II) is generally up to the extent of 25% in commercial samples.

Kraft [6] originated the dehydration of castor oil in 1877. Although Scheiber [6] in 1913 dehydrated the fatty acids of the castor oil, and esterified them with glycerine to give dehydrated castor oil, yet this process remained unattractive for its technicalities. Ufer [13] later on developed certain patents for the direct dehydration of castor oil using acidic salts. The use of Japanese acid clay or fullers earth [7] impregnated with sulphuric acid has been described as successful catalysts. Darkening of the colour and polymerisation to some extent are the drawbacks in most of these processes. However, Ghaneim [8] and Prilutskaya [9] claimed freedom from both these shortcomings by the use of ion-exchange resins. In the present studies an attempt has been made to develop a continuous process for the dehydration of castor oil using locally available clays either as such or impregnated with various ions. Variations, such as the catalyst, its temperature, and feed rate of the oil have been studied. The quality of the product was determined by physical and chemical evaluation.

EXPERIMENTAL

Preparation of the bentonite catalyst

(a) *Acid treatment of the clay*. Sulphuric acid (50%, 2000 ml) was added to bentonite (1800 g) placed in a 5 litre round bottomed flask and refluxed for 30 min. using a heating mantle. After cooling, the contents were transferred to a shallow dish to avoid gelling of the clay. The clay was recovered from this mixture by filtration and was washed with water till almost free from sulphate ions. It was then dried at $100-120^\circ$ for 2 hrs. and was ground if necessary to obtain particles of mesh size 24-60.

(b) *Coating of the clay with various ions*. The dried clay (1.0 kg) was weighed into a stainless steel tray. A concentrated solution of the salt containing 5% salt on the basis of clay taken, was added to it. Additional water if required for adequate soaking was added and mixed thoroughly. The tray was placed in an oven, the temperature was raised slowly to the required degree and maintained for 4 hrs. The mesh size of the catalyst was between 24-60.

Dehydration of the oil

A stainless steel tube (3.5 cm. dia and 30 cm. long) tapered and plugged with glass wool at the lower end was filled with the catalyst. The tube was held vertically in a salt bath containing heat transfer salts (KNO_3, $NaNO_3$, $NaNO_2$). The salt bath was heated electrically to the desir-ed temperature. Castor oil was fed at the top of the catalyst. The rate of the feed was maintained with the help of a droping funnel and the product was collected from the bottom of the tube.

Analysis of the Product

Iodine value of the product was determined by Wijs's method [10]. Hydroxyl values and acid values were determined according to standard procedures [11]. The extent of the diene conjugation [12] was determined by diluting a weighed quantity of the oil and recording its absorption with the help of a spectrophotometer. A U-tube viscometer was used for viscosity determination.

The results are given in the Tables 1-4.

DISCUSSION

Acid treatment increases the porosity of the bentonite clay by dissolving out the acid soluble contents such as alumina, iron, calcium and magnesium etc. The time of the refluxing of the clay with acid is important. Too much refluxing renders the clay which is mostly silica powdery, while shorter reaction times do not bring about the desired porosity. Drying of the acid treated clay at 110° shows no noticeable increase in the dehydrating properties. In order to attain maximum dehydration and effective unsaturation with this clay the catalytic bed had to be maintained at 270°. The product obtained was viscous and highly coloured. In contrast the same acid treated clay when activated at $280-285^\circ$, brings about the same result at a lower temperature ($200-210^\circ$) and the product is also of agreeable colour.

As should be clear from Tables 1-4 the temperature of the bed is an important variable. The iodine value of the product increased with the increase in the temperature of the catalyst bed and attained the maximum value at about 210°. The acetyl value follows a similar pattern and was found to be minimum with the products of maximum unsaturation. But the diene value does not conform to this pattern. In a series of temperature variations, it reached a maximum earlier than the maximum of unsaturation.

Activated clay coated with 5% aluminium sulphate, when used as a catalyst, causes considerable decomposition of the product obviously resulting in an increased acid value. The product is also viscous and slightly dark brown because of charring. Activated clay coated with 5% sodium bisulphate is very efficient catalyst. It increases the iodine value of the product but at the cost of higher acid value and viscosity. However, the product is of fair colour. Activated

Table 1. Activated bentonite as a catalyst.

S. No.	Temp. ($^{\circ}$C)	Flow rate	Iodine value (Wijs)	Acid value	Diene value	Acetyl value	Viscosity in centistokes at 100°F
1.	180	1.00 ml/min	108.6	7.8	5.606	60.24	241.335
2.	190	1.00 ml/min	112.0	10.7	10.644	52.8	271.034
3.	200	1.00 ml/min	119.1	15.4	10.688	40.177	286.946
4.	210	1.00 ml/min	121.2	18.6	6.784	38.53	365.445
5.	220	1.00 ml/min	120.8	21.4	5.478	42.10	455.267
6.	210	0.75 ml/min	122.8	21.9	8.453	30.90	460.327
7.	210	1.50 ml/min	116.4	14.3	8.673	46.18	350.486

Table 2. Activated bentonite coated with 5% $Al_2(SO_4)_3$ as a catalyst.

S. No.	Temp. ($^{\circ}$C)	Flow rate	Iodine value (Wijs)	Acid value	Diene value	Acetyl value	Viscosity in centistokes at 100°F
1.	180	1.00 ml/min	109.20	13.24	3.200	41.04	241.335
2.	190	1.00 ml/min	122.14	16.31	3.633	38.86	271.034
3.	200	1.00 ml/min	125.41	20.16	3.564	37.60	286.946
4.	210	1.00 ml/min	125.65	24.07	3.267	33.86	365.445
5.	210	0.75 ml/min	127.55	21.42	3.929	30.85	276.480
6.	210	1.50 ml/min	119.01	18.52	3.259	35.42	264.462

Table 3. Activated bentonite coated with 5% $KHSO_4$.

S. No.	Temp. ($^{\circ}$C)	Flow rate	Iodine value (Wijs)	Acid value	% Diene conjugation	Acetyl value	Viscosity (centistokes)
1.	180	1.00 ml/min	114.23	10.53	3.399	42.13	249.288
2.	190	1.00 ml/min	117.96	11.20	3.409	41.56	271.034
3.	200	1.00 ml/min	123.25	12.61	3.633	36.52	265.426
4.	210	1.00 ml/min	123.96	13.40	3.608	33.76	280.518
5.	220	1.00 ml/min	122.83	17.64	2.637	35.50	329.244
6.	210	1.50 ml/min	114.05	12.82	2.578	37.83	266.410
7.	210	0.75 ml/min	124.44	14.56	2.968	29.81	284.486

Table 4. Activated bentonite coated with 5% $NaHSO_4$.

S. No.	Temp. ($^{\circ}$C)	Flow rate	Iodine value (Wijs)	Acid value	% Diene conjugation	Acetyl value	Viscosity in centistokes at 100°F
1.	180	1.00 ml/min	128.05	13.36	9.682	27.80	299.951
2.	190	1.00 ml/min	129.40	13.72	10.634	27.63	328.848
3.	200	1.00 ml/min	133.13	14.80	8.542	26.10	324.125

(Table 4, continued . . . . . .)

4.	210	1.00 ml/min	134.34	22.45	4.863	27.35	542.068
5.	220	1.00 ml/min	132.40	25.31	4.829	30.24	549.245
6.	210	0.75 ml/min	133.25	25.76	5.678	25.91	590.378
7.	210	1.50 ml/min	122.41	19.64	3.742	33.43	520.478

clay coated with 5% potassium bisulphate, when used as a catalyst is also good in raising the unsaturation. The product obtained in this case has a slightly low acid value as well as viscosity. The colour of the dehydrated product is slightly brown.

The iodine value decreases with the increase in the flow rate of the oil feed. The hydroxyl groups of ricinoleic acid molecules associate and result in the higher viscosity of the product. By the removal of the hydroxyl group and the introduction of double bond, the viscosity of the product should decrease. In our studies the viscosity increased with an increase in the operating temperature and this is only due to the polymerisation of the dehydrated product. Raw castor oil has a low acid value but it goes on increasing with the rise in temperature irrespective of the nature of the bed. This is of course the result of increasing thermal decomposition and splitting of the oil during dehydration. The fact is more pronounced with clays coated with sulphate ions.

Uncoated activated bentonite clay when used as a catalyst keeps the acid value low, the oil of acceptable colour and less viscous. The diene value is also slightly high.

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