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Addition Reaction of Maleic Anhydride with Conjugated Acid from Vegetable Oils for Synthesis of Polymeric Surfactants

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Abstract: ***Maleic anhydride along with phthalic anhydride and can be used for modification and the modified oil is known as malenized oil was synthesized by Diels alder reaction and the other reaction is direct addition. The malenized oil then evaluated for physicochemical properties such as molecular weight (Mw), foam Volume (ml), Surface tension (ρ) and HLB ratio by standard methods. The malenized oil was studied by IR sepectroscopy, NMR spectroscopy and molecular weight by viscosity methods. The IR and NMR spectral study shows the presence of ester, ether, free hydroxyl and free acid group in malenized oil. The results suggest that the malenized oil found to be useful in formulation of liquid and powder detergent. Malenised vegetable oils have been used in various industrial products like wall finishes, water thinnable paints, electro deposition paints , water thinnable primers, and printing inks.***

Keywords: Malenized oils, liquid and powder detergent

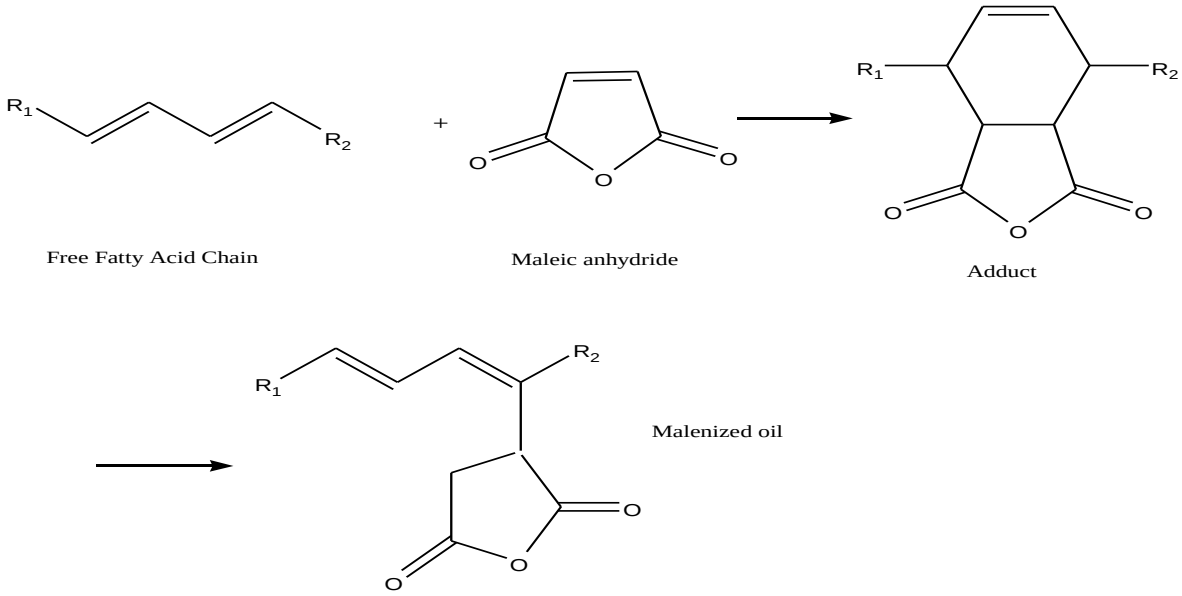
1. Introductions

A number of methods have been suggested for improving the properties of drying oils which involve the separation of the better-drying from the poorer drying components (segregation), the shifting of non-conjugated double bonds to conjugated form (isomerization) and the removal of water to introduce a new double bond (dehydration). There is another method of adding unsaturated compound to the unsaturated part of the oil molecule, thus increasing its complexity and heat reactivity. The compound referred to is Maleic treated or Malenized oil[1]. Maleic anhydride along with phthalic anhydride and can be used for modification and the modified oil is known as malenized oil.

Since the maleic is added near the unsaturation section of the fatty acid radical it retards oxidation slightly so that maleic treated oils do not show greatly increased air-drying properties. However they are definitely faster bodying and have better colour and at equal viscosity and better water resistance in the dried films. Maleic anhydride is a dibasic acid which reacts with both conjugated and isolated double bonds. The possible chemical reactions are addition reaction of Maleic anhydride. When we heat the oil, a part of linolinic acid is converted to 9, 11, 13-octadecatrionoic acid by isomerisation; this conjugated acid reacts with Maleic anhydride by Diels alder reaction[2]. The other reaction is direct addition of Maleic anhydride at active methylene group.

Malenised vegetable oils have been used in various industrial products like wall finishes[3], water thinnable paints[4], electro deposition paints[5] water thinnable primers[6] and printing inks[7]. We have already used malenized oil for production of liquid detergent[8] as well as lotions. Polymeric surfactants are an exciting new addition to the existing product range of surfactants.

In this paper, experimental conditions have been worked out for getting malenized oil based mainly on linseed oil, coconut oil and maleic anhydride. The interaction between conjugated acid with Maleic anhydride (fig.1) and the experimental conditions has studied by molecular weight, HLB ratio and detergency characteristics, IR spectroscopy and NMR spectroscopy. Novel catalysts sodium bisulphate, sodium bisulphate and hydrochloric acid have been used in preparation of malenised oil.



2. Experimental

Materials

All reagents and solvents for synthesises were commercially available and used without further purification. Other chemicals employed were of analytical grade and doubly deionized water were used in all solutions.

Synthesis of Malenized Coconut oil

Coconut oil was treated with different proportion of maleic anhydride and phthalic anhydride to get polymerized maleic modified oils. The major ingredients are linseed oil, maleic anhydride and coconut oil. 1.5% sodium bisulphate, 0.5% sodium bisulphite and 1% hydrochloric acid were used as catalysts. Initially linseed oil, coconut oil, maleic anhydride and catalyst were taken in glass reactor. The mass was heated slowly and steadily to 200^0C in about half an hour. This temperature was maintained for one hour. The reaction temperature was then raised to 230^0C and reaction was continued steadily for two hours at this temperature. Now steadily reaction temperature was lowered down to 150^0 C and the reaction was continued at this temperature for two hours. The acid value and viscosity was observed periodically and reaction was terminated when desired acid value and viscosity has attained. Batch was withdrawn carefully and weighted to get % yield. These oils were neutralized with NaOH, KOH, Diethanolamine and tetraethnolamine. This neutralized oil was later used as an active ingredient in liquid and powder detergents compositions.

Table 1: Composition of Malenized Oil (% by weight)

Ingredient	M-1
Linseed Oil	60
Maleic anhydride	10
Coconut Oil	20
Phthalic anhydride	05
Citric Acid	02
Benzoic Acid	01
Oxalic Acid	02

Physicochemical Analysis of Malenized Oil

Analysis of Malenized oils were carried out by determining acid value[9], saponification value[10], viscosity[11], pH value[12], molecular weight[13], hydrophilic lipophilic balance (HLB)[14], foam height[15] and % detergency[16]. Analysis of of malenized oil is given in Table 2.

Table 2: Physicochemical Properties of Malenized Oil

Oil	AcidValue	Color	Consistency	HLB	Molecular weight	Viscosity	pH
M-10	35.01	Brown	Thin	17	4071	270	2.39

Spectroscopic Study of Malenized Oils[17-20]

Infrared Spectroscopy

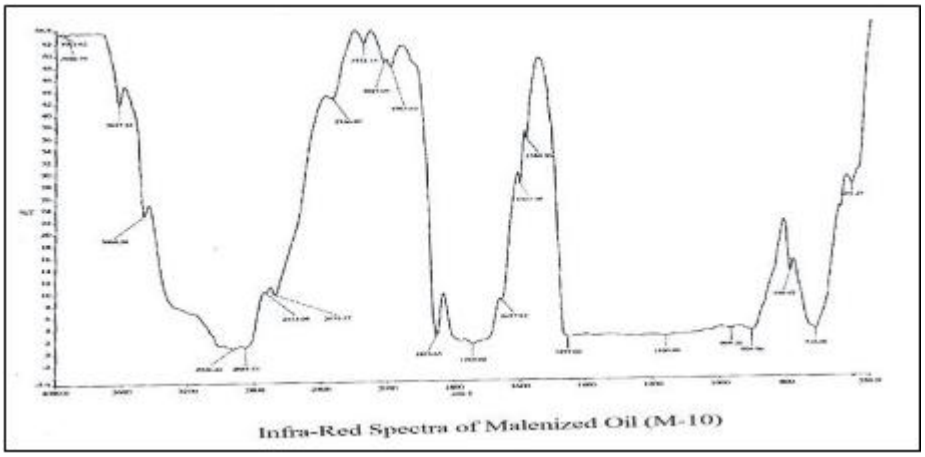


Figure 2: Infra Red Spectra of Malenized Oil (M-1)

Table 3: The prominent peaks of the IR Spectra of Malenized Oil

Malenized Oil	C-H stretch	C=O stretch	C=C stretch	C-O stretch	C-H Bend
M-10	2926.25	1743.02	1660	1160.43	713.06
Literature Value	2500-3000	1700-1750	1620-1860	1070-1250	700-900

Nuclear magnetic resonance spectroscopy

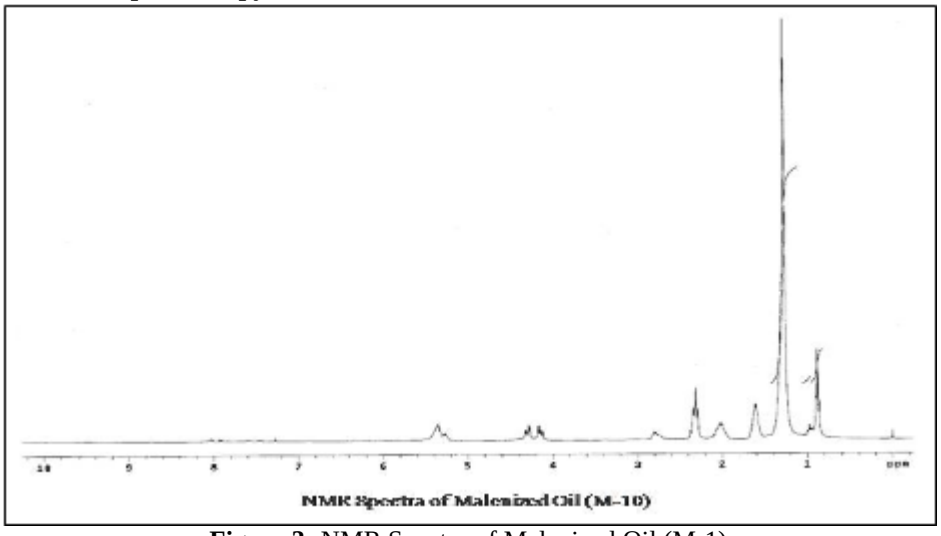


Figure 3: NMR Spectra of Malenized Oil (M-1)

Table 4: The NMR-spectral data of Malenized Oil

Malenized oil (M-1)	Types of Proton	Literature Value(ppm)
0.9	R-CH_3 (primary)	0.9
1.3	R_2-CH_2(aliphatic)	1.3
1.6	R_3CH (aliphatic)	1.5
2.3	HC-COOR (Ester)	2-2.6
2.8	HC-OR (Ether)	3.3-4
4.2, 4.3	RCOO -CH (ester)	3.7-4.1
5.3	C=CH (vinylic)	4.6-5.8
7.3	Ar-H(Aromatic)	6-9

3. Results and Discussion

1) Malenized Vegetables oils have been used in water thinnable wall finishes, paint stainers, detergents, creams and lotions. In the present work, a combination of linseed oil and coconut oil has been used. Linseed oil having very high iodine value (175-190) can find enough sites for Malenized reaction. Coconut oil has a specialty of low molecular weight fatty acids with low percentage of unsaturated fatty acids. This will helps to form more compact and hard polymer which is lathering freely. Incorporation of other acids like phthalic will give an aromatic moiety to the polymer. Thus, a combination of aromatic and aliphatic skeletons will certainly give good properties to active ingredients. A small quantity of 2% of oxalic acid and citric acid has included with the hope that they will give good cleansing stain removing and other desirable chacteristics of detergents. Benzoic acid (1 to 2%) has been included in the formulations to work as a chain stopper as vigorous reaction of maleic anhydride can give high molecular weight which are not desirable.
2) The Physicochemical properties of Malenized Oils are reported in Table 2. The acid value of composition is 35.01 .
3) The samples have a reasonably high viscosity measured by Ford cup no.4. The higher viscosity indicates that polymerization has occurred to the desired extent.
4) The pH value of sample is lower showing that all samples are showing acidic character.
5) Molecular weight is as determined by viscosity method gives molecular weight 4071. This molecular weight of

3000 to 4000 is quite ideal for polymer to work as polymeric surfactants and active ingredients.

6) The Sample has a very high H.L.B. ratio (Based on saponification value) which indicates the suitability of this product as a detergent active materials.
7) From IR and NMR studies show that the presence of primary, secondary and tertiary alkyl groups. These reveal the prepared product has appreciable extent of long chain alkyl groups. Degree of unsaturation in malenized oil is very minor as peak corresponds to C=C stretching is very weak. The protons with ether and ester linkage are prominently observed. The presence of these groups indicates malenization of oil through condensation of –OH groups.

4. Conclusion

Linseed oil and coconut oil can be modified to get malenized oil with desired acid value, viscosity and HLB value. Malenized oil synthesized using linseed oil and coconut oil has huge potential and can be used as substitute for petroleum based actives like Linear Alkyl Benzene Sulphonate and sodium lauryl sulphate. A combination of Hydrochloric acid, sodium bisulphate, sodium bisulphite as catalyst give excellent results. The higher acid value of malenized oil is helpful in making water thinnable composition. Malenized oil is neutralized by sodium hydroxide and potassium hydroxide. However, neutralization of oil by potassium hydroxide, gives excellent result.

The physicochemical analysis like HLB value, viscosity, clarity and color of malenized oil strongly indicates its application for detergent compositions. The Molecular weight of the samples is ideal for using as a polymeric surfactant. The study indicates the possibility of pilot scale and commercial scale production of malenized oil. This malenized oil can be prepared with simple equipment.

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