ECOFRIENDLY MALENIZED OILS FOR LIQUID DETERGENT

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Abstract

The availability and price of crude petroleum is challenging Indian economy seriously. We must think of some basic solutions to this problem. Our industrial and household products like detergents, paints, printing Inks, lubricants, cosmetics are all based on crude petroleum. Our laboratory has taken a serious note of this situation and we have made scientific efforts to replace petroleum products with products of vegetable origin. In this paper, concentrating on one modification of vegetable oil by the process of malenization. In fact it is quite simple to modify vegetable oils like linseed oil, and coconut oil by treatment with Maleic anhydride. The conditions for the preparation of malenized oil in terms of mole ratio of reactants, temperature and catalyst have been synthesized. The malenization of oils has also been tried by microwave synthesis. The results are promising and the reactions can be completed in 3 to 5 minutes. These malenised oils have been compared with standard active materials like linear Alkyl benzene sulphonate and Alpha olefin sulphonate. The malenized oils can successfully replace Acid slurry and Alpha olefin sulphonate to the extent of fifty to seventy percent. Liquid detergents based on malenized oils have been formulated and analyzed for various characteristics like foaming, detergency and stain removing. Malenized oils appear to be a promising substitute for crude petroleum based active materials.

Keywords: Malenized oils, liquid detergent.

INTRODUCTION

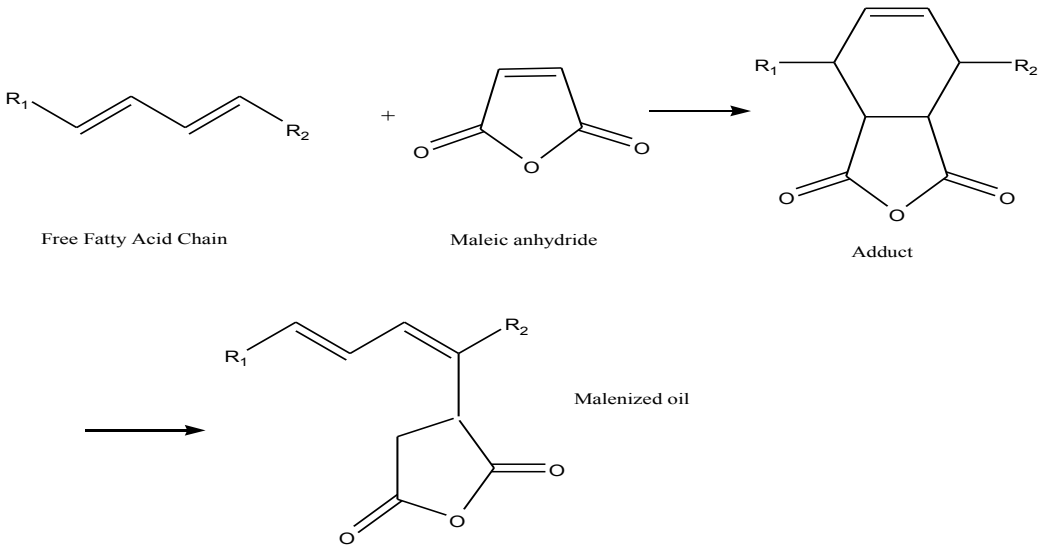
A number of methods have been suggested for improving the properties of drying oils which involve the separation of the better-drying from the poorer drying components (segregation), the shifting of non-conjugated double bonds to conjugated form (isomerization) and the removal of

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 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.



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

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

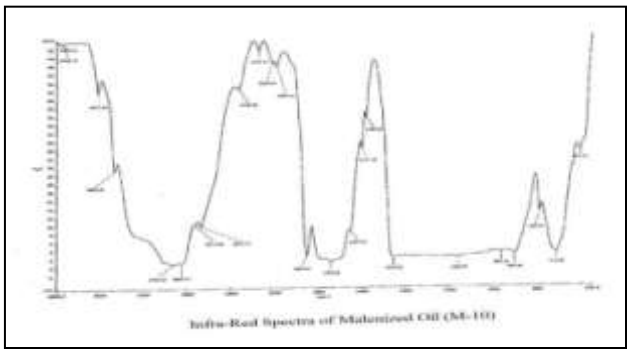


Table 3: The prominent peaks of the IR Spectra of Malenized Oil

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

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

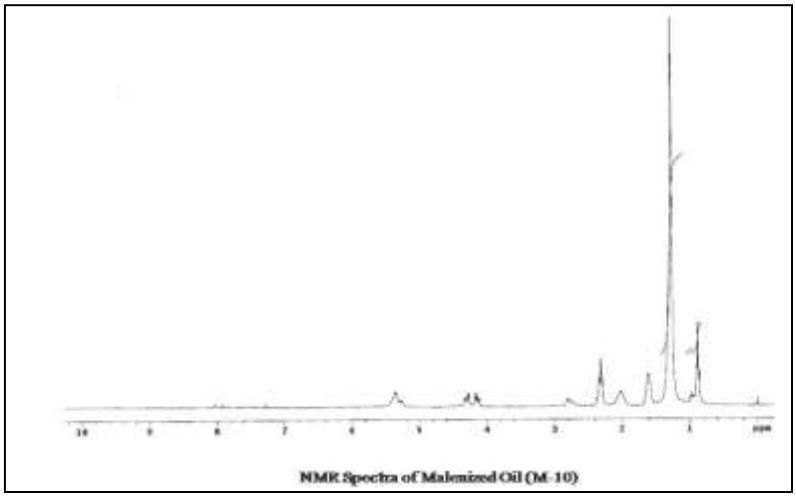


Table 4: The NMR-spectral data of Malenized Oil

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

Table No.5:- liquid detergent based on malenized oil

Sr.No	INGREDIENT	LD1	LD2	LD3
1	Sorbitol	10	10	10
2	Glyerine	10	10	10
3	Urea	03	03	03
4	Alpha olefin sulphonate	02	02	02
5	Malenized oil (100% solids)	--	4.5	9.0
6	isopropanol	01	01	01
7	Water	54	54.5	55
8	Acid Slurry	10	05	-
9	Sodium lauryl sulphate	10	10	10

Table No.6:- Physicochemical properties of Liquid & Commercial Liquid Detergent

Conc.	Sample	Foam volume in CM^3 (time in min.)				Density (gm/cc)	Surface Tension (dyne/cm)
		0	5	10	15		
0.5%	LD1	700	600	550	500	0.794	24.65
	LD2	600	550	550	500	0.799	36.62
	LD3	550	450	400	350	0.812	39.45
	CD1	600	550	400	300	0.851	23.63
1%	LD1	750	750	700	700	0.8308	32.59
	LD2	700	700	650	600	0.99	35.18
	LD3	650	650	550	500	0.99	35.68
	CD1	700	650	400	350	0.99	24.62

Abbreviation: - LD-Liquid Detergent, CD-Commercial Detergent

Table No.7:- Effect of Liquid detergents on% Detergency with 1%solution

Cloth	Medium for Staining	% Detergency by liquid detergent			
		LD1	LD2	LD3	CD1
Cotton	Soil	89.00	87.00	84.00	91.20
	Spinach	85.00	82.50	82.50	89.62
	Tea	62.16	64.86	56.78	76.84
	Coffee	77.14	65.78	76.56	74.52
Polyester	Soil	86.50	84.92	80.62	88.12
	Spinach	85.00	80.12	80.62	89.62
	Tea	66.14	66.66	66.12	79.60
	Coffee	75.14	63.05	69.12	82.12
Terricot	Soil	84.68	83.69	81.74	86.65
	Spinach	83.77	81.62	79.62	88.60
	Tea	69.66	64.92	69.60	81.62
	Coffee	72.62	62.30	66.32	80.69

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.

8. The composition of liquid detergents is given in table no.5. The malenized oil M-1 have been used in liquid detergent compositions in the ratio of 50 and 100%.
9. The samples have foaming characteristics equivalent to commercial sample the reduction in surface tension is also appreciable and comparable to commercial sample. The special features of formulation are freedom from petroleum based actives.
10. The soiling removing characteristics on different cloths are shown in table no.7.At 1% concentrations for terricot cloths, our samples have detergency of 82 to 86% which is comparable to commercial liquid detergents. With cotton and polyester cloths the detergency at 1% concentrations is 84 to 90% which is nearer to the results of commercial products.

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. The study indicates the

possibility of pilot scale and commercial scale production of malenized oil. This malenized oil can be prepared with simple equipment and small scale liquid detergent industry can be made self sufficient to some extent.

References

Y.H. Hoi, (1996). Baily's Industrial oil and fats products, *John Wiley and Sons*, Inc: New York, 5, 78-80.

A.C. Francis and J. R. Richard, (2008). *Advanced Organic Chemistry Part B*, Springer Publication, 5, 473-475.

B.W. Phate and B.B Gogte, (2005). *Paint India*, 3, 71.

P. G Gajbhiye and B.B.Gogte, (2005). *Chemical Engg. World*, 40 (5) ,92.

R. Lambourne, (1987). *Paint and surface coatings*, Theory & practice, ellis horwood limited, New York, 440.

S. K Kharkate and B.B Gogte, (2005). surface coating Australia, 42,4, 91.

V. D. Sawant, (2000). Paint India, 50 , 79-80.

Irja, and Piirma, (1992). polymeric surfactants, surfactant series, Marcel Dekker Inc, New York, 42.

ASTM Standard Method, (1981). For Acid value of organic coating materials, Published by the *American Society for testing materials*, 6.01D; 1639-70.

ASTM standard method,; (1979). For Saponification value of Drying oils, 16.03 D, 952-67.

ASTM standard Method,; (1982). For Viscosity of Paint, Varnishes and lacquers, Resins etc. by Ford cup method, 6.01, D1200-82.

G. H. Jeffery, J. Bassett, J, Mendham, and D. C. Denny, (1989). Textbook of quantitative Chemical Analysis, *Longman Scientific and Technical*, John Wiley and Sons, Inc. New York, 5.

Encyclopedia of Polymer Science and technology, John Wiley and sons, (1982). 1(9); 182-191.

S. J. Jellinek, (1982). *Encyclopedia of Chemical Technology,*; John Willey and Sons, New York, 20,780.

H.E. Garrett, (1972). Surface Active Chemicals, Pregamon Press, New York.

Haries, *Detergency Evaluation and Testing,* Wiley Interscience Publisher, 954, 92-103.

R.M. Silverstein, (1991). *Spectrometric Identification of organic compounds*, John Wiley and sons, Inc., 5, 300-306.

P.S. Kalsi, (1999). *Spectroscopy Identification of Organic Compounds*,.; New Age International Publisher Ltd.,4, 21-41.

. W. Dudley, (2001). I. Fleming, *Spectroscopic Methods in Organic Chemistry*, Tata Mc Graw – Hill Publishing Company Ltd. 4, 42-52.

A.D. Cross, and R. A. Jones, (1969). An Introduction practical I. R. Spectroscopy, Plenium Publishing Corporation, 3, 84-86.