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Preparation of Maleinized Castor oil (MCO) By Conventional Method And It's Application in the Formulation of Liquid Detergent.

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Abstract: Castor (*RicinusCommunis L.*) seed oil has found wide application in the coatings, cosmetics & detergents.India is the largest exporter of castor oil in the world.35-55% of the seed content is a valuable drying oil with many industrial applications.In the present study, modification of castor oil through the melainization of castor oil carried out with the use of maleic anhydride to form maleinized castor oil.In this method of addition of unsaturation compound to the unsaturated part of the oil molecule, thus increasing its complexity and heat reactivity.The product obtained from maleic addition is known as the adduct which when neutralized with inorganic alkali, ammonia gives water miscible oils. Their solubilized oils may be used for different applications like cosmetics,detergents etc. The application of melainized castor oil has been done in the formulation of liquid detergent Liquid detergents prepared by this resin with acid slurry in different proportions are giving excellent results in comparison with that of commercial products.This research was undertaken to develop products which are based on naturally available raw materials specifically not of petroleum origin .This is an attempt to make the novel products useful for society and to reduce percentage of non-renewable product usage in day to day life thus solving problem of environmental pollution to some extent and thus favor eco-friendly products technology.

Keywords: Castor oil; Maleinized Castor oil ; Liquid Detergents ; Maleic anhydride.

1.Introduction[1-5]

Castor (*RicinusCommunisL.*) is cultivated around the world because of commercial importance of its oil. Castor grows best under tropical conditions. It is extensively cultivated in a few states in India namely, Rajasthan, Gujarat and Andhra Pradesh which have suitable climatic conditions. India produces on an average, around 800,000 tons of castor seeds annually, accounting for about 75% of the total world production. Brazil and China constitute the balance global castor seed production. In recent years however, Brazil and China have experienced stagnation in castor crops. In India, castor is planted during July/August and harvesting commences

around December/ January. The castor seed and its oil can be stored for long time without affecting its quality. The Indian variety of castor oil has an oil content of about 48%. The castor seed products are oil and cake, where the oil has large industrial uses like paints, lubricants, pharmaceuticals, textiles, plastics etc. and the cake is used as organic manure in agriculture field.

The castor bean contains 50-55% oil. The oil itself contains a number of fatty acids similar to those in cooking oils, such as oleic acid, linoleic acid, stearic acid and palmitic acid. However, among vegetable oils, castor oil is distinguished by its high content (over 85%) of ricinoleic acid. No other vegetable oil contains so high a proportion of fatty hydroxyacids. Castor oils unsaturated bond, high molecular weight (298), low melting point (5^0C) and very low solidification point (-12^0C to -18^0C) make it industrially useful, most of all for the highest and most stable viscosity of any vegetable oil (Bonjean, 1991).

2. Market And Market Potential[1-5]

Castor oil is sold either for pharmaceutical or industrial use. Specification for pharmaceutical use can be found in the European Pharmacopeia. The industrial type may be divided into first, second and third quality. Only pressed castor oil, extracted without solvents, can be called first quality. These oils, produced in Europe, are virtually colourless and have very low acidity. Second and third quality oil are commercial names, meaning that the oil has been extracted using solvent.35-55% of the seed content is a valuable drying oil with many industrial applications.

The primary use of Castor oil is as a basic ingredient in the production of nylon 11, sebacic acid, plasticizers and jet engine lubricants, nylon 6-10, heavy duty automotive greases, coatings and inks, surfactants, polyurethanes, soaps, polishes, flypapers, paints, varnishes, lubricants, and many other chemical derivatives and medicinal, pharmaceutical and cosmetic derivatives.

The plant is also used for fibre, an insecticide and repellent. Cellulose from the stems is used for making cardboard and paper products.

The oil from the seed is a very well known laxative and purgative that has been widely used for over 2,000 years. It is so effective that it is regularly used to clear the digestive tract in cases of poisoning. The oil has a remarkable antidandruff effect. The oil is well tolerated by the skin and so is sometimes used as a vehicle for medicinal and cosmetic preparations. Castor oil congeals to a gel-mass when the alcoholic solution is distilled in the presence of sodium salts of higher fatty acids. This gel is useful in the treatment of dermatitis and is a good protective in cases of occupational eczemas and dermatitis. Medicinal applications consume a tiny fraction of total production.

Table No:1-Properties of Castor oil:

Density (20 ^{o}C)	**0.956 - 0.963 g/ml**
Viscosity (20 ^{o}C)	9.5-10.0 dPa.s
Refraction index n2d	1.477 -1.479
Saponification value	177- 187
Iodine value	82 – 88
Unsaponifiable matter	0.3 -0.5%
Hydroxyls	160 minimum

3.Aim and Objective of Present Research Work[1-5]:

The present work is aimed at developing the Oleo-chemicals based on Castor oil which can be used in liquid detergents. In the first stage of the work, preparation of Maleinized Castor oil has been standardized by choosingproper ratio of reactants, time of heating and cooking schedule to get desirable properties. This Maleinized Castor oil is used as substitute of conventional ingredients in liquid detergents. Thus, several formulations of liquid detergents have been attained in which a part of Acid Slurry has been replaced with Malenized Castor oil.

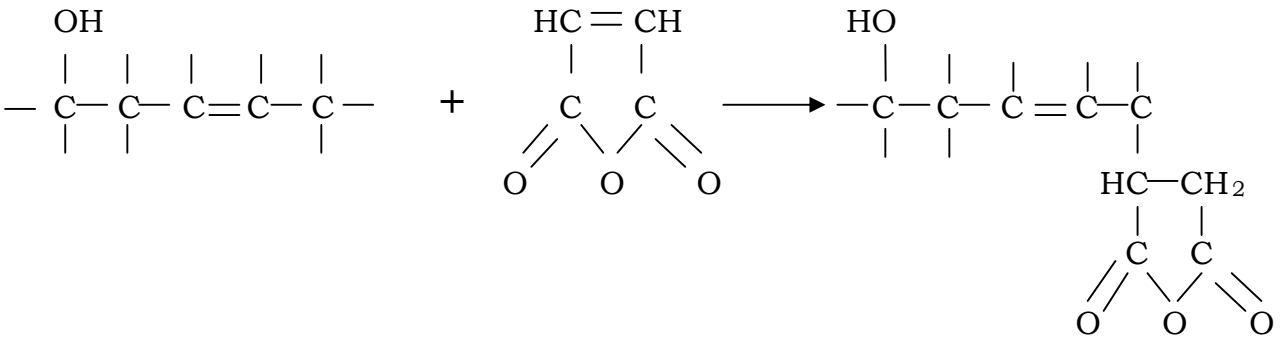
This research is undertaken with the objective to develop products which are based on naturally available raw materials specifically not of petroleum origin .This is an attempt to make the novel products useful for society and to reduce percentage of non-renewable product usage in day to day life thus solving problem of environmental pollution to some extent.

4.Malenized Castor Oil

A number of methods have been suggested for improving the properties of drying oil which involve the separation of better drying from the poorer drying components (segregation), removal of water to introduce a new double bond (dehydration).

There is a method of adding unsaturation compound to the unsaturated part of the oil molecule, thus increasing its complexity and heat reactivity. The compound referred to is maleic anhydride and the oils are known as maleic treated or Maleinized oils. Since the maleic is added far or 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 color and at equal viscosity, better water resistance in the dried fillers.

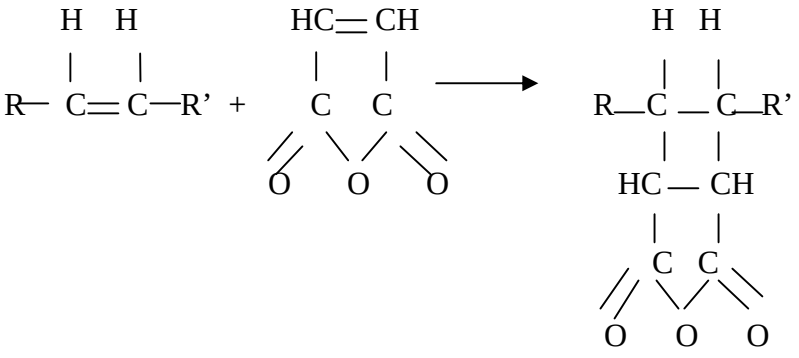
Maleic Anhydride: - It is a dibasic acid, which reacts with both conjugated and isolated double bonds in the following manner-



The product obtained from maleic addition is known as the adduct which when neutralized with inorganic alkali, ammonia or amine gives water miscible oils. Their solubilized oils may be used for different applications like cosmetics, water paints of emulsion type disinfectants etc. based on the amount of maleic allowed to react with the oil. Usually 10-25% of maleic anhydride is sufficient to produce the desired increase in neat reactivity in the non-conjugated oils. However, up to 15% maleic is made to form an adduct with the unsaturation portion of the fatty acid radicals in drying oils to get optimum desirable properties.

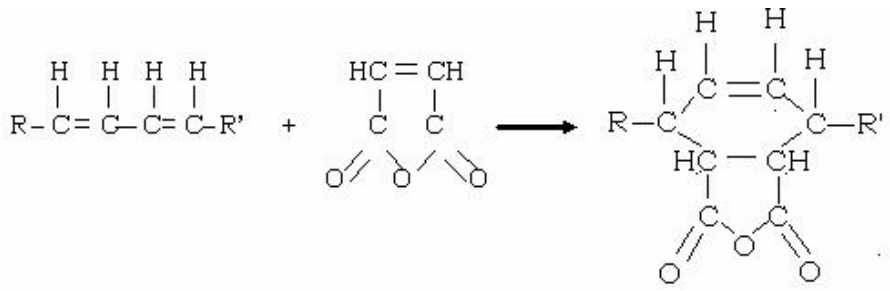
5.Mechanism Of Adduct Formation:

Clocker in U.S. patent 2,275,843 proposed that additions of maleic takes place at double bonds as follows:



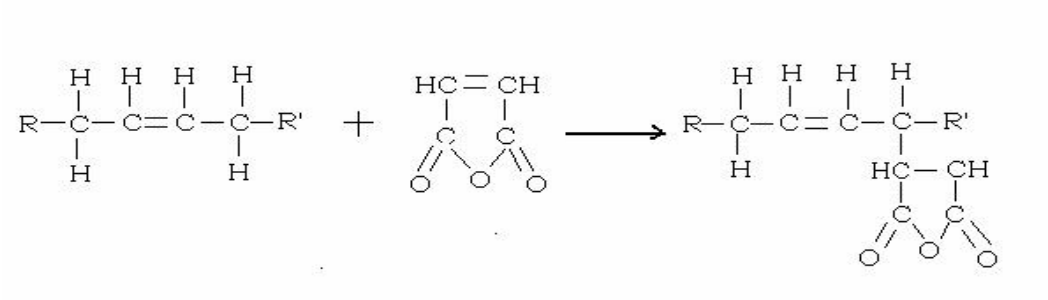
However, this mechanism does not appear to be likely because it would be difficult to form a four-member ring under specified conditions and this type of ring structure is not very stable.

A Diels- Alder type of addition is entirely possible for oils with conjugate unsaturation.



This type of reaction does not take place with oils having non-conjugated unsaturation unless the conditions are such that the oil isomerizes to the conjugated form during the reaction. Wheeler Et Al has stated in the studies of maleic treated methyl ester type of isomerization and addition occurs with methyl linoleate and maleic anhydride.

From this result, they concluded that transfer of a hydrogen atom from the fatty acid chain to the maleic anhydride formed a substituted succinic anhydride as follows;

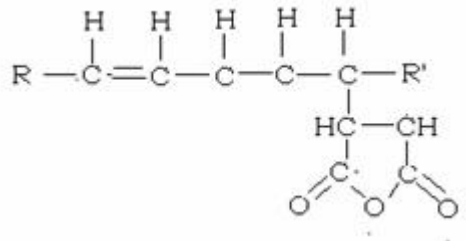


Wheeler et al also found that the first molecule of maleic anhydride reacting with methyl linoleate reacts mostly to saturate one double bond, and the second one adds without affecting the unsaturation, in addition, they also found that the first two molecules of anhydride reacting with methyl linoleate react mostly to saturate one double bond each, and the third molecule adds without affecting the unsaturation. The unsaturation was determined by the Wij's iodine method, and it was recognized that this method is not accurate if conjugated unsaturation has been formed. Therefore these works for the linoleate and linoleate adducts gave no structures.

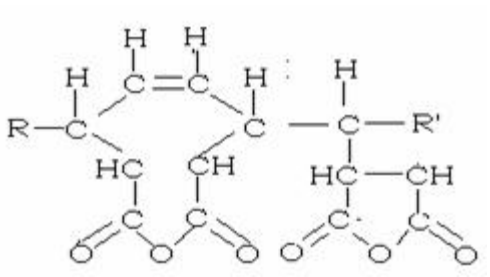
Kappelmeir believes that, with oleic radicals, the addition takes place as indicated above with the formation of a succinic anhydride derivative without affecting the double bonds.

With the linoleic esters, the first molecule adds to form the succinic anhydride derivative and shift in the unsaturation occurs to form the conjugated type. The second molecule of maleic anhydride then adds to the conjugated unsaturation occurs to form the conjugated type. The second molecule of maleic anhydride then adds to the conjugated unsaturation by the Diels-alder type of reaction. Therefore the structure obtained from the addition of one and two molecules of maleic would be as follows :

One molecule of maleic added:



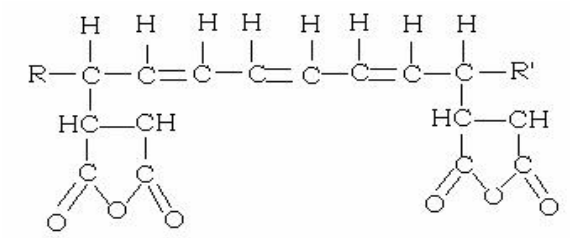
Two molecules of maleic added:

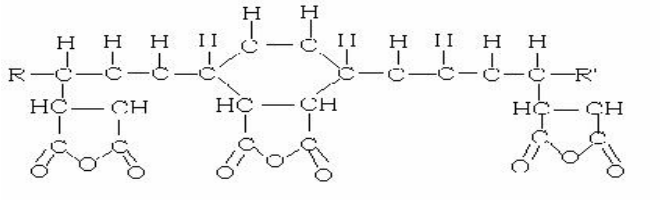


In case of the linoleic radicals Kappelmeir believes that a molecule of maleic anhydride may be added simultaneously to both ends of the unsaturated portion with the consequent formation of a triple conjugate system. This would be followed by the addition of a third molecule of maleic anhydride may be added simultaneously to both ends of the unsaturated portion with the consequent formation of a triply conjugate system.

This would be followed by the addition of a third molecule of maleic by a Diels-Alder mechanism to give the structure shown below:

Two molecules of maleic added:





Three molecules of maleic added:

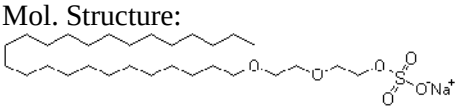
Kappelmeir describes a possible method for determining the extent of the maleic addition from the fact that dimethyl aniline forms a highly coloured product with free maleic anhydride.

6. Materials and Methods[1-5]:

Chemicals Required: Wij's solution, KI, water, Sodium indicator, carbon tetrachloride,0.5 Nalco. KOH, 1% phenolphthalein indicator, 0.5 N hydrochloric acid, Neutral alcohol 0.1 N, Phenolphthalein Indicator, Oxalic acid, 0.1 N Alco. KOH

Apparatus: Conical flask burette, pipette, balance, water bath & heater,Flat bottom flasks (250 ml capacity), reflux condenser, burette, balance,I.V. bottles,Ford cup No. 4 , refractometer.

Table No:2-Various raw materials were used in this project. Their properties, grades and sources are tabulated below-

Raw Materials	Grade	Source	Properties
Castor oil	—	—	Specific Gravity:0.958 Boiling pt.: 0.950 to 0.970 Refractive Index:1.4790 Sap value:176-187 Iodine Value: 83-89 Acetyl value:150 Unsaponifiable matter:0.3 to 0.37
KOH	Laboratory chemical	S.D.Fine Chemicals	Appearance: White deliquescent solid Specific Gravity: 2.04 pH: 13.5 (0.1 molar solution) Boiling Point: 1320 ^{0}C Melting Point: 360^{0}C
Sorbitol	Laboratory chemical	Samar Chemicals	Physical state and appearance: Solid Molecular wt.:182.17 gm/mole Boiling Pt.:decomposes Melting pt.:111.5^{0}C Sp. Gravity:1.489
Tween-20	Laboratory chemicals	Ranbaxy fine chemicals	Mol. Formula: $C_{18}H_{34}O_6$ Mol. Wt:346.5 Boiling pt: 100^{0}C Density: 1.11 gm/ml at 20^{0}C Refractive Index:1.468
SLS	—	—	Mol. Formula: $CH_3(CH_2)_{10}CH_2OOSOONa$ Mol. Wt.:288.38 gm/mole Colour : Whitish to yellow Melting pt:204^{0}C
SLES	—	—	Mol. Structure:  Mol.wt.376.48 Mol. Formula: $C_{12}H_{25}O(C_2H_4O)_2SO_3Na$

7. Experimental Setup:

Experimentation has been done in following stages –

1)Analysis of castor oil was done by determination of it's acid value (A.V.) , Saponification Value(S.V.) , Iodine value(I.V.), Acid Value(A.V.), viscosity, refractive index, density, color and consistency…etc.

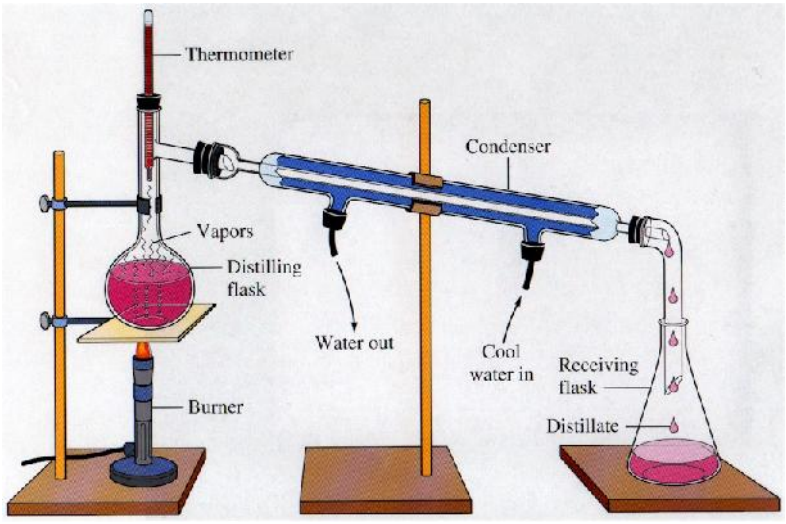
2) Saponification byConventional method

3) Maleinization of castor oil:

a) Analysis of Maleinized oil

b) Applications of Maleinized castor oil

THE REACTOR SETUP



Saponification process of castor oil :

Conventional process : Weigh 100 gms Of Castor oil .According to its sap. Value, weigh KOH (dissolved in minimum amount of water) .Add 2-3 ml. of neutral alcohol to this KOH. Add this alco. KOH solution to the sample & heat the mixture for 1-2 hrs. till the mass becomes homogenous. Mixing of two layers shows that the saponification is complete.

Analysis of Saponified oil :

After saponification process, the sample was checked for its solubility in water. Mass which is completely soluble in water and forms a turbid solution with water is said to be completely saponified.

8.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 clamp

2) Methodology & Cooking Schedule Of Maleinized Oil Synthesis: The reaction, temperature & addition of ingredients are detailed below;

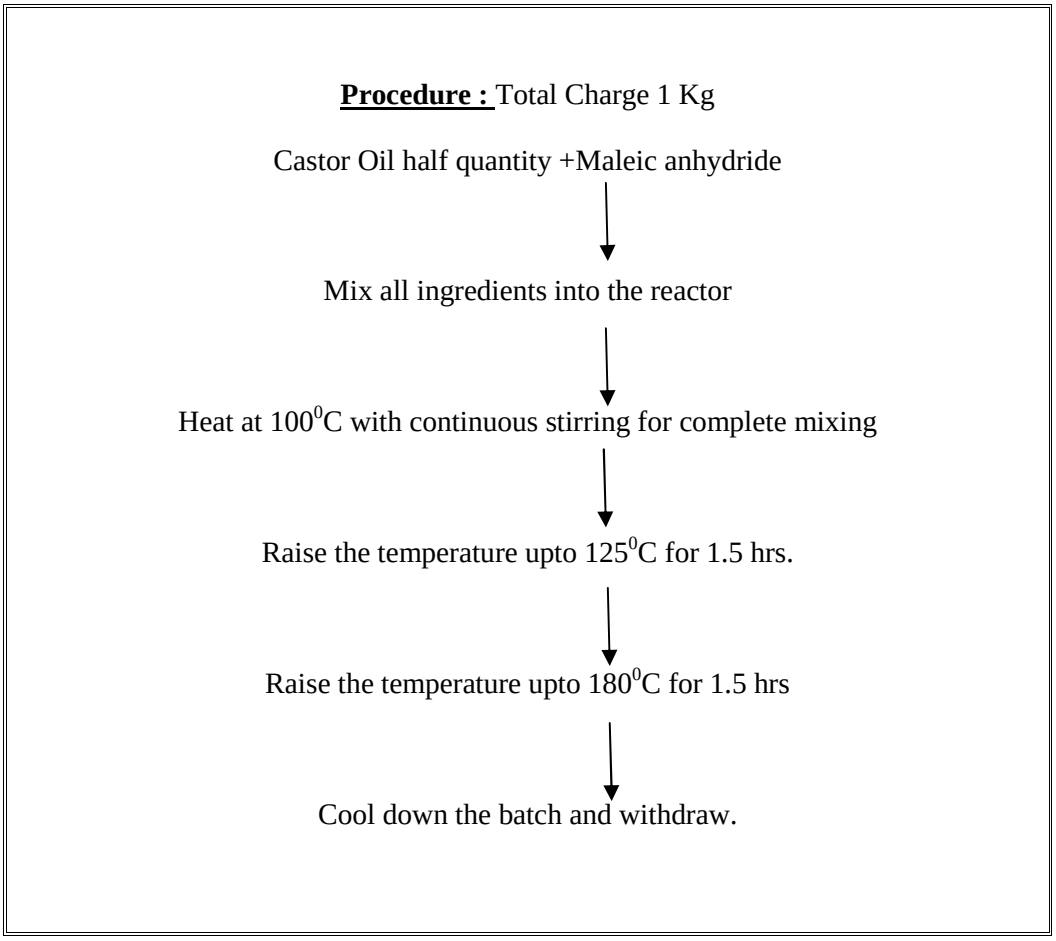
Step 1) Maleic Anhydridewas added in approximate quantity of castor oil to form a slurry. **Step 2)** The slurry was then introduced in the reactor and heated with agitation to a temp. of 100 ^{0}C in 1 hr.

Step 3) The slurry was further heated for one and a half hour at 125°C

Step 4) Heating was continued for another one and a half hour at 180°C.

Step 5) 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.

Flow-sheet No:1



9. Application of Maleinized Castor Oil in Liquid Detergents:-

To use the preparedmaleinized oil in a liquid detergent it is necessary to neutralize it by using Triethanolamine so that its acid value becomes zero. Neutralized maleinized oil prepared by above method is used in the liquid detergents having composition shown in the table below. This resin is used in the liquid detergent in various proportions with acid slurry and analyzed for its effect on the properties such as foam height, surface tension etc.

Table No:3-Formulation for Liquid Detergent.

Sr. No.	**Raw materials**	**Composition (% by weight)**				
		I	II	III	IV	V
1)	Acid slurry	8	12	16	0	10
2)	Neutralized resin	12	8	4	20	10
3)	NaOH	4.4	4.4	4.4	4.4	4.4
4)	TSP	6	6	6	6	6
5)	Urea	12	12	12	12	12
6)	SLES	12	12	12	12	12
7)	Water	145.6	145.6	145.6	145.6	145.6

Analysis of liquid Detergents:-

Liquid detergents were analyzed for the moisture content, foam height and surface tension as per standard methods.

10. Results& Discussion

Results of different analysis done in present project are tabulated below.

Table No.:4-Analysis of Castor oil.

Sr.No.	Properties	Value
1	Sap. Value	180
2	Iodine Value	85
3	Refractive Index	1.4790
4	Specific Gravity	0.958
5	Color & Consistency	Dark yellow and viscous

Table No.:5-Analysis of Maleinised Castor oil (M.C.O.).

Sr.No.	Properties	Value
1)	Acid Value	40.07
2)	Sap. Value	284.6
3)	Iodine Value	72.6
4)	Refractive Index	1.487
5)	Density	0.985
6)	Colour & Consistency	Dark Brown
7)	HLB Value	12.8

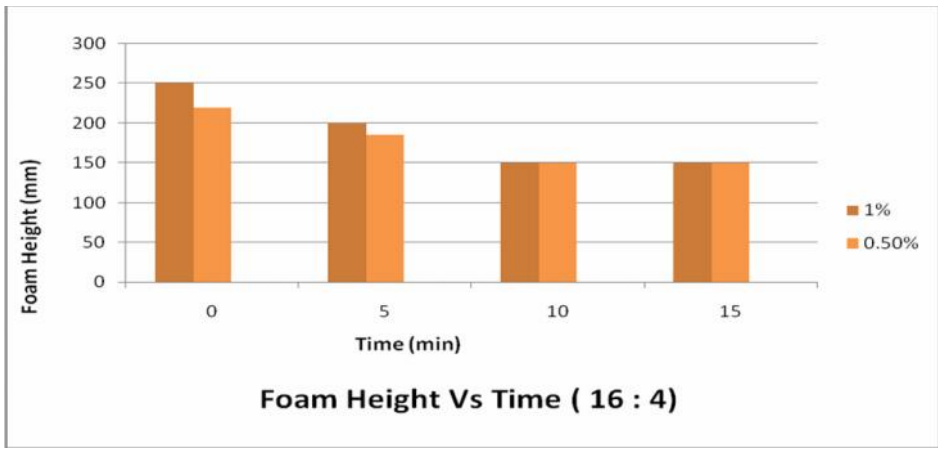
Table No.6-Analysis of Liquid Detergents.

Sr. No.	Properties		I 8:12		II 12:8		III 16:4		IV 0:20		V 1:1	
1)	% Solid Content		**31.4**		**32.4**		**33.6**		**32**		**32.1**	
2)	Foam Height	% solution	1	0.5	1	0.5	1	0.5	1	0.5	1	0.5
		i) 0 min.	0	0	350	260	250	220	0	0	320	250
		ii) 5 min.	0	0	130	200	200	185	0	0	140	150
		iii)10 min	0	0	120	170	150	150	0	0	120	100
		iv) 15 min.	0	0	120	170	150	150	0	0	100	100
3)	Surface tension (dyne/cm)		-	-	55.1	55.3	70.3	84.6	-	-	59.2	60.2
3)	pH		7.5		7.5		7.5		7.5		7.5	

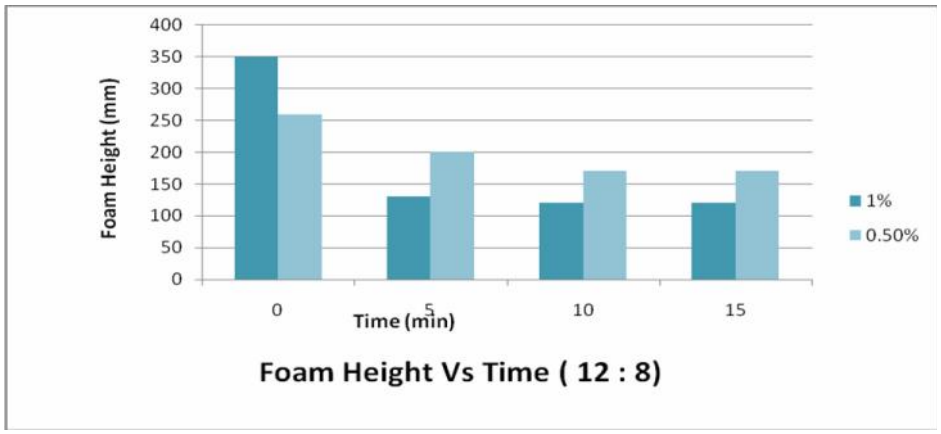
Table No.7-Analysis of commercial Detergents

Composition	% conc.	Foam Height				Surface Tension (dyne/cm)
		0	5	10	15	
Surf Excel	0.5	340	315	295	270	36.944
	1	390	370	345	315	29.160
Nirma	0.5	310	295	270	255	36.909
	1	360	335	300	275	30.253

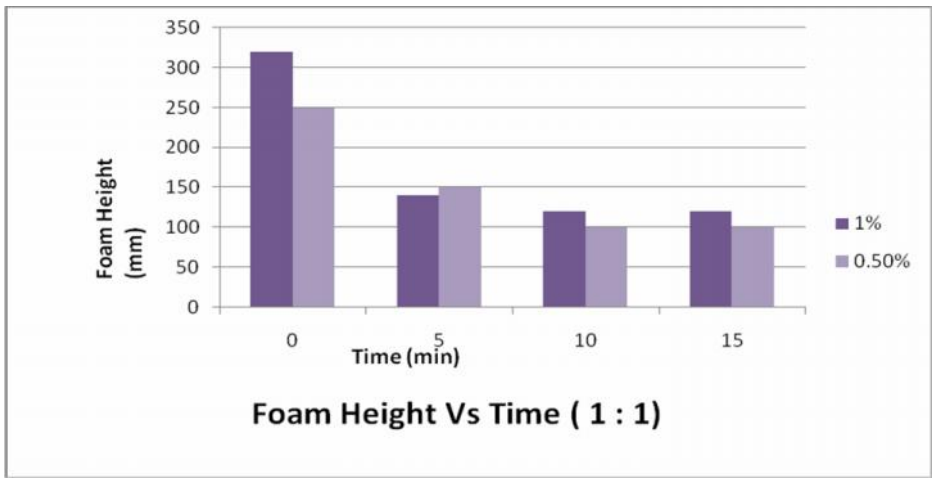
Graph No.1



Graph No.2

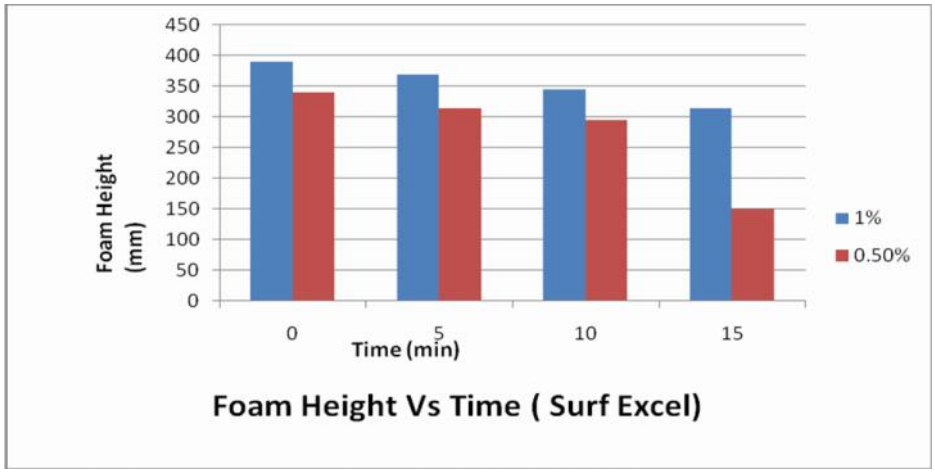


Graph No.3

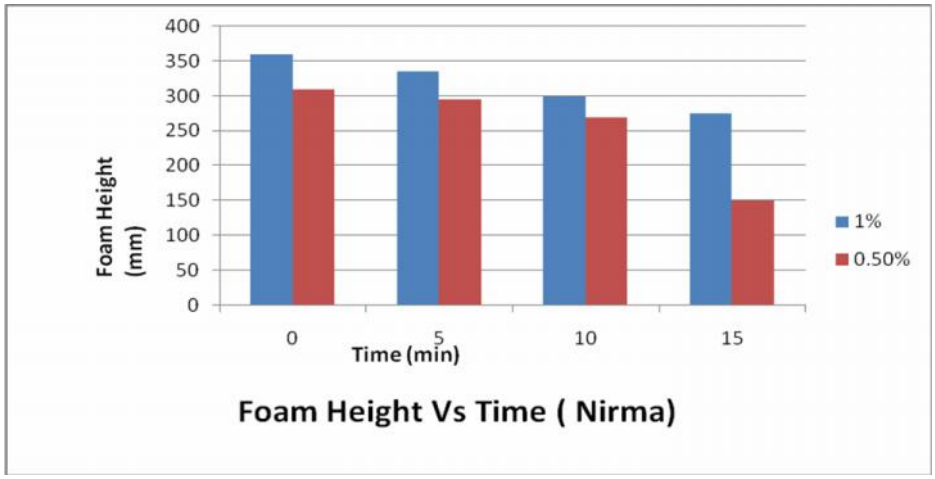


Commercial Products:

Graph No.4



Graph No.5



12.Conclusions:

1. Saponification of castor oil is carried out to a greater extent by the conventional method.
2. Maleinized castor oil has been prepared using maleic anhydride and castor oil for improvement in its properties like acid value, viscosity etc.
3. Petroleum jelly, mineral oil and lanoline can be replaced by maleinized castor oil. So our products are eco-friendly.
4. Liquid detergents prepared by above resin with acid slurry in different proportions are giving excellent results. Some of them like I, III & V are having stable foam, while formulations II & IV form foamless detergents.

13. References:

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