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The Manufacture of Sulfonated oil and The Determination of The Wetting Power and The Surface Tension of Its Emulsions

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The Manufacture of Sulfonated Oil and The Determination of the Wetting Power and The Surface Tension of Its Emulsions

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中文摘要

應用蓖麻油，芝蔴油，花生油及棉籽油製造紡織工業用磺酸化油之試驗，經多次之試製，已得一較圓滿之方法，其成品之成份，根據A. O. C. S. 方法，加以分析，其各種濃度乳化液之濕潤度及表面張力，亦經測定，並與C. T. I. 乳化油(中紡公司外貨乳化油非植物油製成者)及NOPCO. 1067(美國製品)乳化液逐一比較，得一結論如下：

(1) 由試驗示知各種植物油製得之磺酸化油乳化液，其表面張力，相差甚微，其濕潤度之强弱，以蓖麻油，芝蔴油，花生油及棉籽油之次序排列。

(2) NOPCO. 1067 爲極佳之濕潤劑，其濕潤度及表面張力均屬最優。

(3) C.T.I. 乳化油，其表面張力，與由植物油磺酸化油相近，其濕潤度則僅優于磺酸化棉籽油。

是以磺酸化蓖麻油，芝蔴油，花生油，均可代替C. T. I. 乳化油，供紡織工業之應用。

INTRODUCTION

Sulphonated oil is an important wetting agent. It is manufactured by the action of concentrated sulphuric acid on oils and fats. This wetting agent is extensively used in treating the cotton fiber for dyeing and printing with Turkey-Red, so it is commonly called by the name of Turkey Red oil. It is also used in leather finishing.

Wetting agents are generally prepared by hydrophobic hydrocarbon chain plus one or more strongly hydrophilic groups. On sulphonated oil, the hydrophilic group SO_3H or SO_4H is introduced into the chain of aliphatic fatty acid. The nature of fatty acid reaction with concentrated sulphuric acid is not fully understood yet. Juillard, Bogajewsky & Benedikt had stated different opinions on it.

In general, this reaction is not a true sulphonation, simply because the sulfur atom does not combine with the carbon atom directly as sulfonly group and the product is easily decomposed by boiling with hydrochloric acid. No matter how complex the reaction is we should

consider that it is simply an esterification or addition reaction.

In this respect, we should state out that according to the fatty acids composition, castor oil, neat's foot oil and cod oil are most suitable for sulphonation. Other vegetable oils, such as seasame oil, peanut oil and cottonseed oil may be also used in this manufacture.

The percentages of essential fatty acids in some of these oils are tabulated as follows:

	Castor oil	Peanut oil	Sesame oil	Cotton seed oil
Saturated fatty acid	1.8-3%	18.4%	12.2%	21.9%
Oleic acid $C_{18}H_{34}O_2$	7-9	58	46.0	32.15
Linolic acid $C_{18}H_{32}O_2$	3-3.5	20.7	25.2	39.35
Linolenic acid $C_{18}H_{30}O_2$	—	—	—	—
Ricinoleic acid $C_{18}H_{34}O_3$	80.86	—	—	—

Jamieson: Vegetable Fats and Oils, 2nd. edition.

There is one OH group in the ricinoleic acid, so the action of concentrated sulfuric acid on it is considered as esterification.

Owing to the unsaturation of oleic acid and linolic acid the actions upon them may be considered as addition reaction.

All these products either from esterification or from addition are soluble in water and have emulsifying property.

Our aim of this experiment is to determine the wetting power and surface tension of different concentrations of sulphonated oil emulsion. The reactions of the sulphuric acid on fats or oils are not discussed in this paper.

There are two factors which have great influence on the wetting power of the wetting agents. One is the solubility and the other is the balance position. The former means the degree of hydrophilic property, which is depend upon the nature of the hydrophilic group, the length of the chain and the number of double bonds in a molecule. The latter means the balance position of hydrophilic group with hydrophobic group on one molecule.

On account of this, the high unsaturation of the reacting materials are not sure to be good wetting agents, because the large number of double bonds in the molecules are not arranged in a balanced position. On the other hand the castor oil is a best raw material of sulphonated oil, as its main component, ricinoleic acid, has an OH group and one double bond, which is just in a balanced position.

Draves method is commonly used to determine the wetting Power of a wetting agent. It was designed by Draves and Clarkson and has been accepted by the American Association of Taxtile Chemists and Colorists, It is to determine the time required for a 5-gram skein of

two ply unboiled cotton yarn weighed with a sinker, to submerge in the solution under test The time of sinking is an indicator of the wetting qualities. When these values are plotted on a log-log scale paper as a function of wetting agent concentration, a straight line relation is obtained.

(The standard five gram skeins of 2-ply cotton yarn suitable for this test may be obtained from Hooker and Sanders, 40 Worth St., New York, N. Y. U. S. A.)

In our experiments, we use the commercial yarn as testing material. Owing to the degree of compactness of the skein, we do not get a perfect data of the sinking time. But the comparative values could be used as reference to textile industry.

Leveling power of a wetting agent is roughly related to its surface tension, the smaller the surface tension the more effective as a leveling agent. We use Du Nouy Tensiometer to measure the surface tension of each solution.

EXPERIMENTAL

(1) The analysis of raw materials:

In this experiment. we used four kinds of vegetable oils, namely, castor oil, sesame oil, peanut oil and cottonseed oil. These oils a.e produced in large quantities in North China. Their constants have been analyzed in this laboratory as listed in Table: I.

Table I. The analysis of raw materials:

	Castor Oil (Refined)	Castor Oil (Comm.)	Sesame (Refined)	Peanut (Comm.)	Cottonseed oil (Comm.)
Unsaponifiable matter	0.82%	2.0%	1.50%	0.79%	1.0%
Specific Gravity	0.9585	0.9519	0.9172	0.9129	0.9158
Refractive Index	1.4821	1.4824	1.4777	1.4769	1.4729
Iodine Value	82.1	82.0	108.2	88.3	96.6
Saponification Value	187.7	189.8	194.1	191.8	200.2
Acid Value	3.94	5.66	0.19	1.73	0.54

(II) The preparation of sulphonated oil:

The most satisfaotory procedure for the preparation of sulphonated oil based on our experiments is as follows:

Add 30 grams of concentrated sulphuric acid (sp. gr. 1.84) dropwise into 100 grams of oil with constant stirring. Keep the temperature below 35° C. The stirring should be continuous. The total period of stirring should be not less than four hours. The viscosity of the oil increased gradually. When a sample of the oil taken out from the batch can be emulsified completely, pour the mass into Glauber's salt solution, whose concentration should

be 10-13° Be. After stirring well, put into an electric oven. (Keep the temp. between 40°-50° C.) for several hours until it separates clearly. Syphon out the water layer. The volume of Glauber's salt solution used for washing is two times as much as that of the oil. In order to remove the unreacted acid completely the above process should be repeated.

After washing, neutralize the mass with 10 % 30° Be caustic soda solution and 90% 13° Be Glauber's salt solution mixture. Use Congo Red as indicator. The alkalinity of the resulted mass may contain 0.2-0.3% Na_2O, Let it stand in an electric oven (40° C.) over night.

(III) Analysis of sulphonated oil:

There are two methods to test and evaluate the sulphonated oils. One is by chemical analysis and other, by practical examination. The analytical data are tabulated as follows:

Table II. The analysis of sulphonated oils

	Sulfonated cotton seed oil (comm.)	C.T.I. Soluble Oil	Sulfonated castor oil (refined)	Sulfonated castor oil (comm.)	Sulfonated sesame oil (refined)	Sulfonated peanut oil (comm.)
Moisture	2.44%	28.36%	24.06%	19.75%	18.15%	7.76%
Ash	0.737	3.16	5.42	4.61	3.83	0.92
Total fatty matter	92.2	37.15	65.36	71.10	74.17	89.85
Combined SO_3	1.29	2.25	5.495	3.43	2.08	1.49
Free SO_3	0.36	0.25	0.685	0.55	1.20	0.50
Total alkalinity ($\%Na_2O$)	0.006	0.567	0.011	0.012	0.009	0.018

"C. T. I. Soluble oil"—This soluble oil is sent by The China Textile Industry Co. Tientsin Factory. We have been requested to evalute and find a substitute for it.

(IV) Practical examination of sulphonated oil:

The general practical examination of sulphonated oil, is to mix a sample with ten volumes of water. When completely emulsified shows no oily drops, it should not separate after standing over night. In our experiments, all can pass this test except the sulphonated cotton seed oil. The characteristics of these emulsions are tabulated in Table III.

(V) The wetting power of sulphonated oil emulsions:

The wetting power of sulphonated oil emulsion was determined by Draves method Its procedure and apparatus used will be stated as follows: (Figures 1 and 2)

For the preparation of emulsions of sulphonated oils for tests 10 grams of sample is aken to make a 10 g/L. stock solution. Then dilute to 0.1, 0.5, 1.0 & 2.0 g/L. solution.

Wind a 5.0 grams skein (20) yarn to a loop of 18 inches. The hook with its

Table III. General characteristics of sulphonated oil emulsions: (concentration: 10 g/L.)

	NOPCO. 1067	C. T. I. Soluble Oil	Sulfo. Castor oil (refined)	Sulfo. Castor oil (comm.)	Sulfo. sesam oil (refined)	Sulfo. peanut oil (comm.)	Sulfo. cotton seed oil (comm.)
Color	yellow	milky white	greenish white	greenish white	pale white	slightly white	slightly white
Oily drops	neg.	posi.	neg.	neg.	neg.	neg.	posi.
Sediment	neg.	neg.	neg.	neg.	posi.	neg.	neg.
Suspen-sion	neg.	neg.	neg.	neg.	neg.	posi	neg.
Faoms	posi.	neg.	neg.	neg.	neg.	neg.	neg.
Clarity	T.L.	T.L.	T.P.	T.P.	T.L.	T.P.	T.P.

'T.P.'—Transparent, 'T.L.'—Translucent

'NOPCO. 1067'—It is a standard wetting agent of the National Oil Products Co. New Jersay, U. S. A. and is manufactured by the same company.

Figure 1.

A. 3-6 grams Cu. or Ni. hook

B. Fine thread same as samle

C. 40 grams lead anchor.

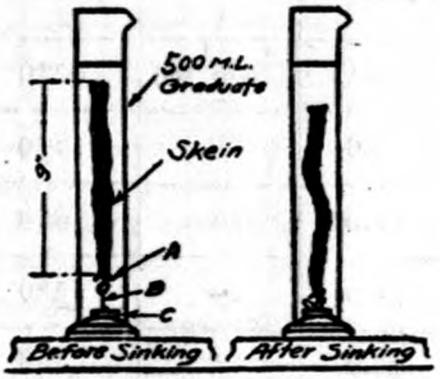


Figure 2.

anchor is fastened to one end of the loop and the other end is cut by shears. The cut end is drawn through the fingers when testing wetting agents in order to make it more compact. The skein is held in one hand with the anchor dangling into the wetting solution contained in a 500 c.c. graduated cylinder. A stop watch held in the other hand is started just as the skein is released into the solution and it is stopped when the buoyant skein definitely starts to sink to the bottom of the cylinder. The skein before sinking must be entirely covered with solution and yet it must posses enough buoyancy from the air within the yarn to keep the thread taut between the anchor and the hook. At least the average of four determinations of sinking time should be obtained for each concentration of wetting agent. The average sinking times of each aulphonated oil emulsions are tabulated in Tables IV & V

(VI) The surface tension of sulpohnated oil emulsions:

Use the above 10 g/L. solution, as stock solution. Dilute to 0.1, 0.6, 1.0, 2.0 g/L solutions. Then determine its surface tension by Du Nouy Tensiometer. Average scale reading was calculated into dynes/cm.

Table IV. The wetting power (sinking time) of sulphonated castor oil (refined) at 25° C.

Concentration g/L	Weight of yarn	Weight of hook	Stare time	Sinked time	Sinking time
0.1	5 gm.	6 gm.	10- 2-0	10-13- 0	780 sec.
0.6	5 ,,	6 ,,	9-20-0	9-21- 0	60 ,,
1.0	5 ,,	6 ,,	9-22- 0	9-22-30	30 ,,
2.0	5 ,,	6 ,,	9- 0-50	0- 0-60	10 ,,
10.0	5 ,,	6 ,,	0- 0-30	0- 0-32	2 ,,

Sinking time with distilled water is 17,666 sec.

Table V. The wetting power (Sinking Time) of sulphonated oil emulsions : at 25° C.

Concentration g/L.	NOPCO. 1067 1	C.T.I. soluble oil 2	Sulpho. castor oil (refined) 3	Sulpho. castor oil (comm.) 4	Sulpho. sesame oil (refined) 5	Sulpho. peanut oil (comm.) 6	Sulpho. cotton seed oil (comm.) 7
0.1	735 sec	5520	780	580	1130	3260	4300
0.6	45	1260	60	75	145	860	2500
1.0	25	660	28	34	85	415	2100
2.0	10	480	13	20	30	230	1740
10.0	2	150	2	3	5	35	1180

Table VI. The surface tension of C.T.I. soluble oil: at 19° C.

Concentration g/L	Scale reading in divisions	r (dynes/cm.)
0.1	96.2	67.52
0.6	85.3	59.75
1.0	76.0	53.22
2.0	72.6	50.88
10.0	67.8	47.55

The following formula was used to calculate the surface tension of a solution.

$$r = \frac{W\,g}{2\,L}$$

r=surface tension of the solution in dynes/cm.

W=weight of liquid raised (gm.)

g=gravity 980 dynes/cm.

L=circumference of the Pt. ring (cm.)

Examle: The surface tension of C. T. I. soluble oil 0.1g/L at 19°

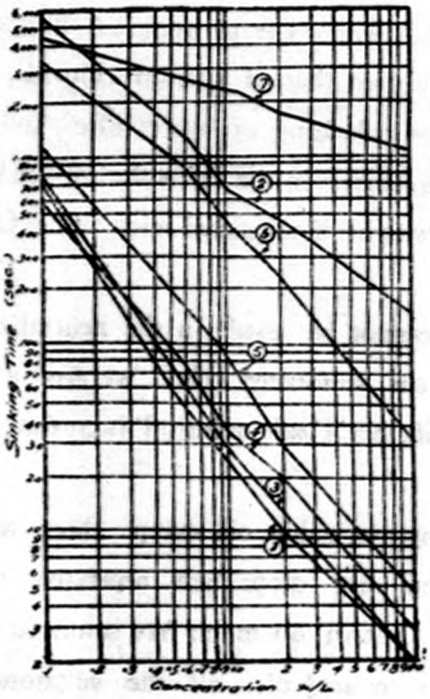
Circumference of the Pt. rig	4.033 cm.
Scale reading in divisions	96.2
Torsion balance cilibration (scale division/gm.)	173.3

$$\text{Force exerted in gm.} = \frac{96.2}{173.3} = 0.555$$

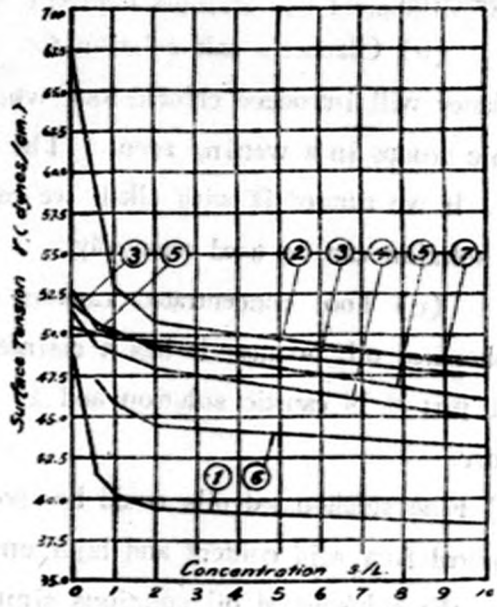
$$r = \frac{W\,g}{2\,L} = \frac{0.555 \times 980}{2 \times 4.033} = 67.52 \text{ dynes/cm.}$$

Distilled water: scale division 105.5 at 12°C.

r=73.93 dynes/cm.



Curve 1. The wetting power (Sinking Tientsin) of sulphonated oil emulsions against its concentrations.



Curve 2. The surface tension of sulphonated oil emulsions against its concentrations

DISCUSSION & CONCLUSION

(I) In the preparation on sulphonated oil we find out three points which offect the yield and properties of the product.

(a) The completion of reaction between oil and sulphuric acid is proportional to the stirring time and speed. longer stirring time and higher speed accelerate the reaction. the temperature should be kept at 35° C. or a little lower. Otherwise the secondary reaction will

Table VII. The surface tension of sulphonated oil emulsions:

r (dynes/cm.) at 19° C.

Concentration g/L	NOPCO. 1067 1	C. T. I. Soluble oil 2	Sulfo. Castor oil (comm.) 3	Sulfo. Castor oil (refined) 4	Sulfo. sesame oil (comm.) 5	Sulfo. peanut oil (comm.) 6	Sulfo. cotton seed oil (comm.) 7
0.1	48.80	67.52	52.85	51.55	52.15	49.95	50.45
0.6	41.70	59.75	50.45	49.45	50.85	47.25	50.10
1.0	40.35	53.22	50.05	49.05	50.45	45.95	49.85
2.0	39.62	50.88	49.45	48.00	49.40	44.50	49.45
10.0	38.52	47.55	47.30	44.62	45.90	43.20	48.70

take place above 35° C. with liberation of sulphurous acid. Too low a temperature will retard the reaction.

(b) Glauber's salt solution for washing is better than that of sodium chloride, because the latter will introduce chlorideion, which influences the balancing of hydrophilic and hydrophobic groups in a wetting agent. The unreacted acid dissolves in the salt solution and separates out. If we titrated it with alkali we can calculate the weight of unreacted acid. The Glauber's salt solution can be used repeatedly.

(c) Too concentrated caustic soda solution cannot be used in the neutralization of sulphonated oil, because it has a disintegration effect on sulfonated oils. we find a mixture of 1 part 8 N caustic solution and 10 part 13° Be Glauber's salt solution is most satissfis factory.

(II) Fine sulphonated oils could be prepared from any vegetable oil except those with high saturated fatty acid content and high unsaturations. The oily drops are separated out oils. from the sulphonated oil solutions simply because they contain too much free saturated fatty oils.

(III) Except the C. T. I. soluble oil & sulphonated cotton seed oil, all the sulphonated oils, have nearly the same wetting power (sinking time) and surface tension The oily drops, sediment, suspension can be removed from its solution by decantation and there will be no further separations.

(IV) The surface tensions of C. T. I. soluble oil at low concentrations are about 10 degree higher than those of the vegetable oils. From the concentration kg/L and up their surface tensions are about the same. The wetting power of C. T. I. solubie oil only ranks higher than the sulfonated cottonseed oil. Therefore it is safe to say that sulfonated castor oil, sesame oil, or peanut oil can be uses as substitute for C. T. I. soluble oil in dyeing.

(V) The chemicial composition of NOPCO 1067 is 50% alkyl-aryl sulfonated and 50%

sodium sulfonate. It is extensively used as wetting agent and detergent in textile industry. whose wetting power is as 60 times as C. T. I. soluble oil. The high penetration power is better than all other oils under examinations. How to prepare the above type of wetting agent, and how to mix a part of the wetting agent into sulphonated oil emulsion to improve its wetting power is a new problem in our laboratory.

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