

# INTERESTERIFICATION OF SARDINE OIL

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In a previous paper<sup>1)</sup> by one of the authors, Y. Toyama, several vegetable oils and fats were subjected to interesterification or molecular rearrangement of glyceride at low temperature<sup>2)</sup> in order to know if this reaction can be used successfully for the preparation of an edible fat from liquid fatty oil or an edible hard fat from low melting fat. In a continuation of the previous study, the authors have examined this reaction for drying oils in an expectation that this reaction will cause the bulk of the saturated acids of glyceride to form tri-saturated glyceride and the winterization after this reaction will yield a winterized oil of high unsaturation suitable for use in paint. In this paper are recorded the results of experiments on sardine oil.

## Experimental and Discussion

*1. Procedures of interesterification.* Unless otherwise stated, a 150 cc gas washer was used as the reaction vessel. Several vessels containing 40-60 g of sample oil added with catalyst were connected in series by a rubber tube and placed in a thermostat. The exit of the last vessel was connected with an oil-seal. Dry nitrogen was passed through the vessels in order to keep a good distribution of catalyst in the reaction mixture and also to keep the reaction mixture out of contact with air. After air in the vessels had been completely replaced by nitrogen, it was not necessary to pass nitrogen through the vessels constantly. Nitrogen was then passed through the vessels at regular intervals. After the specified reaction periods, the reaction mixture in the respective vessels was added with 10% hydrochloric acid with vigorous agitation to destroy catalyst and allowed to stand for one hour at the final reaction temperature. The product was then heated at 130-140°C under a vacuum of 2-5 mm Hg in order to remove xylene which constitutes the bulk of the catalyst used. While both catalysts, a suspension of sodium methylate in xylene and a solution of sodium methylate in methanol, were used in the previous experiments, the former alone was used throughout these experiments in order to avoid the formation of appreciable amounts of methyl esters of fatty acids in the course of interesterification. Since the activity of this catalyst was found to be liable to decrease in the course of storage, the catalyst was prepared anew at several times in these experiments, and the concentration of sodium methylate in the catalyst was determined immediately before use. One cc of catalyst used in these experiments contained 0.046-0.095 g of sodium methylate.

*2. Properties of interesterified oil.* The original sardine oil used in these experiments had acid values 4.4. This oil was alkali-refined, and the refined oil was thoroughly dehydrated by heating at about 100°C under vacuum. The oil thus obtained was subjected to interesterification for 24 hours in total, the reaction temperature being lowered stepwise from 30°C to 0°C in the following manner: 1 hr each at 30°,

25° and 20°C; 2 hrs at 18°C; 4 hrs each at 16° and 14°C; 3 hrs each at 12° and 10°C; 2 hrs each at 8° and 5°C; 1 hr at 0°C. Table 1 shows the properties of interesterified oil obtained by using varying amounts of catalyst. The reaction proceeds to a greater extent yielding an interesterified oil of higher cloud and cold points by increasing the amount of catalyst used. With less than about 0.5% of catalyst, the reaction proceeds only to a very insufficient extent. Increasing amount of catalyst causes the interesterified oil to have higher acid value; especially the oil of Expt. No. 7 shows a considerably higher acid value than the oil of Expt. No. 6 does, while both oils have nearly the same cold point, though the former has a higher cloud point than the latter.

TABLE 1. Properties of Interesterified Oils Obtained by Using Varying Amounts of Catalyst (1)

Expt. No.	Sample oil	Interesterified oil						
		1	2	3	4	5	6	7
Catalyst (%)	—	0.14	0.29	0.43	0.58	0.72	1.00	1.45
Acid value	0.34	1.8	2.5	3.9	4.9	5.2	6.8	11.3
Cloud point (°C)	2	4	13	19	23	24	26	32
Cold point (°C)	-1	0	0	9	18	18	20	20

Since unsaturated acids of glyceride also enter into the reaction, interchange of highly unsaturated and less unsaturated acids between glyceride molecules may occur to some extent. In order to inquire into this sort of interesterification, the oils before and after interesterification in Table 1 were brominated, the ether-insoluble bromides were separated and their Br-content were determined with the results given in Table 2, which indicate that there exists no simple relationship between the yield and Br-content of ether-insoluble bromide and the progress of interesterification, the former varying somewhat irregularly with the latter.

TABLE 2. Ether-Insoluble Bromide

Expt. No.	Sample oil	Interesterified oil				
		1	2	4	5	6
Ether-insol. (Yield (%)	59.93	62.17	62.69	62.47	60.63	62.31
bromide { Br-content (%)	60.03	60.65	61.15	61.95	61.72	62.46

3. *Experiments on winterized sardine oil.* The sample oil described above was gradually cooled down to 5-3°C in the course of 20 hours, and solid was removed by suction filter, yielding a winterized oil (A) in a yield of about 70%. This winterized oil was subjected to interesterification for 26 hours, the reaction temperature being lowered stepwise from 30°C to 2°C. The properties of interesterified oil are given in Table 3. The reaction does not proceed extensively by using catalyst in an amount of less than about 0.5%. Even a prolonged reaction period does not materially favor the progress of reaction if a lesser amount of catalyst is used, for the interesterified oil obtained by 48 hours reaction at 25-0°C using 0.2% of catalyst showed cloud point 0°C and cold point -3°C.

TABLE 3. Properties of Interesterified Oils Obtained by Using Varying Amounts of Catalyst (2)

Expt. No.	Winterized oil (A)	Interesterified oil				
		1	2	3	4	5
Catalyst (%)	—	0.40	0.67	0.80	0.93	1.20
Acid value	0.48	2.8	3.9	4.5	6.2	6.8
Cloud point (°C)	4	20	25	26	26	27
Cold point (°C)	-5	12	16	16	18	23

Another sample of winterized oil (B) prepared from the same sample oil was subjected to interesterification using 0.5% of catalyst, the temperature being lowered from 25°C to 5-4°C, and the reaction period being 24 hours in an experiment and 11.5 hours in another experiment. The results of both experiments are shown in Table 4, from which it is seen that the properties of interesterified oils obtained at the reaction periods of 24 hours and 11.5 hours do not noticeably differ from each other.

TABLE 4. Properties of Interesterified Oils Obtained at Varying Reaction Periods

Expt. No.	Winterized oil (B)	Interesterified oil	
		1	2
Reaction period (hr)	—	24	11.5
Acid value	0.37	3.0	3.0
Cloud point (°C)	-0.5	16	17
Cold point (°C)	-2	5	5

For the sake of comparison, another lot of alkali-refined oil and winterized refined oil (C) were prepared from the original sardine oil, and both oils were subjected to interesterification for 24 hours under the same condition, the reaction temperature being lowered stepwise from 25°C to 0°C. As is seen from Table 5, the winterized oil yields interesterified oils of high cloud and cold points, and the reaction proceeds nearly to the same extent for both oils when more than 0.5% of catalyst is used.

TABLE 5. Comparison of Interesterified Oils from Sardine Oil and Winterized Sardine Oil

Expt. No.	Catalyst (%)	Acid value	Cloud point (°C)	Cold point (°C)
Sardine oil	Before interesterification	—	2	-1
	1	0.28	14	4
	2	0.46	20	9
	3	0.68	24	13
Winterized sardine oil	Before interesterification	—	-3	-6
	1	0.28	-1	-4
	2	0.46	21	10
	3	0.68	21	10
	4	0.91	4.9	27

4. *Winterization of interesterified oil.* Another lot of alkali-refined oil I<sub>a</sub> and winterized refined oil II<sub>a</sub> was prepared from the original sample oil. One kg of each

oil was placed in a 2 l three necked flask equipped with a stirrer, and added with 0.5% of catalyst. Interesterification was performed for 24 hours at 24-6°C by step-wise lowering of temperature in an atmosphere of nitrogen. When the temperature was lowered to 20°C after 9 hours since the beginning of the experiment, the reaction mixture became solid, so that the reaction hereafter was performed without stirring. The properties of interesterified oils are shown in Table 6, in which tri-saturated glyceride is crystalline glyceride which separated on cooling a solution of 10 g of sample oil in 100 cc of petroleum ether at 0°C. Although tri-saturated glyceride is contained in the oils before the reaction in so minute amount that it does not crystallize out from its petroleum ether solution, the amount of tri-saturated glyceride after the reaction may be regarded as the amount of tri-saturated glyceride formed by the reaction. Thus approximately 10% of tri-saturated glyceride is formed by interesterification.

TABLE 6. Properties of Interesterified Oil

	Iodine value (Wijs method)	Acid value	Cloud point (°C)	Cold point (°C)	Tri-saturated glyceride (%)
{Sample oil I <sub>a</sub>	161.7	0.33	3	-1	0
{Interesterified oil I <sub>b</sub>		4.38	29	22	10.4
{Winterized oil II <sub>a</sub>	171.5	0.28	-5	-7	0
{Interesterified oil II <sub>b</sub>		3.95	25	18	8.4

The winterized oils I<sub>b</sub> and II<sub>b</sub> were brought to melting, the melted oils were gradually cooled to 15°C, and solid was removed by suction filter giving the winterized oils I<sub>c</sub> and II<sub>c</sub>. Solid was again melted, and the melted oils were gradually cooled to a temperature of 20°C, at which the liquid (I<sub>d</sub> and II<sub>d</sub>) and the solid (I<sub>e</sub> and II<sub>e</sub>) fractions were separated by suction filter. The yield and iodine value of each fraction are shown in Table 7.

TABLE 7. Winterization of Interesterified Oil

Fraction	I <sub>c</sub>	I <sub>d</sub>	I <sub>e</sub>	II <sub>c</sub>	II <sub>d</sub>	II <sub>e</sub>
Yield (%)	26	29	45	30	25	45
Iodine value	183.1	178.3	139.8	193.1	187.8	148.3

The fractions I<sub>d</sub> and II<sub>d</sub> deposited a large amount of solid and were just mobile at room temperature in winter. Since the fractions I<sub>c</sub> and II<sub>c</sub> also deposited solid at room temperature in winter, they were filtered under vacuum at 4°C, by which the fraction I<sub>c</sub> yielded 86% of winterized oil I<sub>f</sub> having iodine value 191.2, while the fraction II<sub>c</sub> yielded 88% of winterized oil II<sub>f</sub> having iodine value 198.9. Thus winterized oils of very high iodine value are obtainable by winterization of interesterified oils, but their yields are very low. Although repeated winterization of the fractions I<sub>d</sub> and II<sub>d</sub> may yield a further amount of winterized oil which is free from solid at room temperature in winter, it requires much trouble to carry out these procedures. In short, it is easy to form a large amount of solid by interesterification, but it requires a further study on the process of separation in order to obtain a winterized oil suitable for paint oil from interesterified oil in a good yield.

The amounts of saturated acids in the oils winterized after interesterification,

$I_f$  and  $II_f$ , and in the oils before interesterification,  $I_a$  and  $II_a$ , are given in Table 8. For the determination of saturated acids, solid acids in the mixed fatty acids of the oil under examination were determined by means of the lead salt alcohol method, and the content of saturated acids in the mixed fatty acids was calculated from the iodine value of solid acids on an assumption that the acid responsible to the iodine value of solid acids is oleic acid. Comparing the oils winterized after the reaction with the oils before the reaction, it is recognized that the amount of saturated acids is decreased by roughly 10% by winterization after the reaction. This is consistent with the above mentioned fact that approximately 10% of tri-saturated glyceride is formed by interesterification. It should be noted, however, that since over 10% of saturated acids are still found in the oils  $I_f$  and  $II_f$ , the progress of interesterification is far insufficient to separate all of the saturated acids from the glyceride mixture by way of crystallizable tri-saturated glyceride. This is explicable if the relation between the content of tri-saturated glyceride in glyceride mixture and the content of saturated acids in the mixed fatty acids is taken into consideration. The mixed fatty acids which contain 10 mole % of saturated acids, for instance, give rise a randomly rearranged glyceride mixture in which only 0.1 mole % of tri-saturated glyceride is contained. Such a minor amount of tri-saturated glyceride is hardly crystallized out and remains dissolved in the glyceride mixture under the condition of the present experiments, so that the oil obtained by winterization after interesterification still contains saturated acids in an amount of 10 mole % on the basis of mixed fatty acids.

TABLE 8. Amounts of Saturated Acids

Oil	$I_a$	$I_f$	$II_a$	$II_f$
Saturated acids (%) on the basis of mixed fatty acids	24.8	13.2	21.4	10.8

In another experiment, the oil  $I_a$  and its winterized oil  $II'_a$  having iodine value 168.1 were subjected to interesterification. Winterization after the reaction yielded two fractions  $I'_c$  and  $II'_c$  corresponding to  $I_c$  and  $II_c$  in Table 7. The iodine values of  $I'_c$  and  $II'_c$  were 177.1 and 180.6, respectively, and their yields were 70% and 75%, respectively. Since the winterization was not intensely performed, the iodine values of  $I'_c$  and  $II'_c$  were smaller than those of  $I_c$  and  $II_c$ . Spectrophotometric analysis was carried out with the fatty acids of  $I_a$ ,  $I'_c$  and  $II'_c$  in ethanol, and the diene and triene conjugations were estimated with the results shown in Table 9. The amounts of each conjugation in the three samples are equally small, indicating that conjugation of polyethylenic acids does not occur in the course of interesterification.

TABLE 9. Amounts of Conjugations

	Diene conjugation (%)	Triene conjugation (%)	Total conjugation (%)
$I_a$	3.3	0.1	3.4
$I'_c$	2.8	0.2	3.0
$II'_c$	2.7	0	2.7

5. *Drying property of interesterified oil.* A series of drying test was performed with the oils  $I_f$  and  $II_f$  obtained by winterization after interesterification, the winterized oil  $II_a$  without interesterification, a sample of linseed oil for contrast, the boiled oils prepared therefrom by adding cobalt resinate, and the white paints prepared from the boiled oils and zinc oxide. As shown in Table 10,  $I_f$  and  $II_f$ , either of raw oil, boiled oil and white paint, are superior to  $I_a$  and are comparable to linseed oil in their drying property. Another series of drying test was performed with the oils  $I'_c$  and  $II'_c$ , which were obtained by winterization after interesterification and had lower iodine values than  $I_f$  and  $II_f$ , the oil  $II'_a$  and the same linseed oil as used in the experiments of Table 10. The results are shown in Table 11, in which the indoor test was carried out in summer and the outdoor test was carried out in the same season under direct sunlight. The oils  $I'_c$  and  $II'_c$  show a better drying property than  $II'_a$ , but are far inferior to linseed oil. Thus, oils of good drying property can not be obtained if the removal of solid by winterization after interesterification is not intensely effected.

TABLE 10. Drying Test (1)

Oil	Time for drying (hr)					
	Raw oil		Boiled oil		White paint	
	Room temp. 5-18°C	40°C	Room temp. 5-18°C	40°C	Room temp. 5-18°C	40°C
$II_a$	200	163	163	95	52	25
$I_f$	80	40	50	30	25	17
$II_f$	70	38	50	30	25	17
Linseed oil	80	45	52	32	25	18

TABLE 11. Drying Test (2)

Oil	Time for drying (hr)					
	Raw oil		Boiled oil		White paint	
	Indoor	Outdoor	Indoor	Outdoor	Indoor	Outdoor
$II'_a$	290	240	267	216	99	78
$I'_c$	267	216	147	145	96	75
$II'_c$	267	216	147	145	96	75
Linseed oil	67	52	52	49	17	15

### Summary

1. Interesterification of sardine oil or winterized sardine oil at low temperature using a suspension of sodium methylate in xylene as catalyst does not proceed extensively if catalyst is used in a lesser amount than about 0.5% as sodium methylate. By using over 0.5% of catalyst the reaction proceeds to nearly same extent at the reaction periods of 24 hours and 11.5 hours.

2. Roughly 10% of tri-saturated glyceride is formed by the interesterification under the condition described above, the reaction temperature being lowered stepwise to 4°C. But the interesterified oil still contains over 10% of saturated acids in the mixed fatty acids.

3. Conjugation of polyethylenic acids does not occur in the course of inter-esterification.

4. Oils extensively winterized after interesterification, boiled oils prepared therefrom, and white paints prepared from the boiled oils and zinc oxide are comparable to linseed oil, boiled linseed oil and white paint prepared therefrom, respectively, in their drying property.

5. It requires a further study on the process of winterization in order to obtain a winterized oil of good drying property from extensively interesterified oil in a high yield.

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#### References

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