UDC 615.417.2-012.2 : 665.325.2 : 541.18.02

13. Hisakichi Matsumura, Sadao Iguchi, Magobei Yamamoto, and Shigeru Goto : Colloid Chemical Researches on Suspensions in Pharmacy. III. On Rheological Behavior in Rancid Peanut Oil–Aluminum Stearate System.

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In the preceeding paper,[1] the authors pointed out that the mixture of peanut oil and aluminum stearate, which is one of the most widely used vehicles for repository in oily preparation, presented characteristic rheological behaviors, its high rigidity and viscosity being possibly due to the secondary structure in its colloidal system. However, these properties are much affected by the nature of oil used. It may result from changes in chemical properties of the oil by deterioration. Therefore, rancid peanut oil was first selected and its rheological properties when dispensed with aluminum stearate were investigated. In addition, preliminary observations on some other vegetable oils were also made.

Experimental

1) Materials : Peanut, soybean, linseed, and olive oil were all J. P. VI products, and their constants are tabulated in Table II. Aluminum stearate (Al-St) was the same as that used in the previous experiments (Extra Pure Grade of Kwanto Chemical product) and purified similarly.

2) Assay methods for oil : Acid value and saponification value were both determined by the J. P. VI method. Iodine value by the Hanus method, peroxide value by iodovolumetry using starch indicator in accordance with the Wheeler method. Hydroxylamine value is defined, by analogy, as the number of mg. of KOH which is equivalent to the hydroxylamine required to derive the carbonyl function in 1 g. of oil to an oxime. The method adopted was essentially that of Trozzolo and Lieder[2] which has been applied on fixed oils by Nogami, *et al.*[3]

3) Development of rancidification of oil : In the present work, peanut oil was selected for this purpose. Into a Pyrex beaker, fitted with a tube for intake of oxygen, a definite volume of oil under investigation was placed and the beaker was tightly enclosed with transparent polyvinyl chloride sheet**(Mitsui Chemical Product), supported to permit circulation of dry oxygen and irradiation of ultraviolet ray. The beaker containing the oil was then placed in an electric heating oven and maintained at 85° during irradiation by ultraviolet lamp, fixed at 15 cm. over the oil surface. Thus, by bubbling dry oxygen through the oil and irradiation of ultraviolet ray, autoxidation was accelerated further.

The constants of the oils were assayed as mentioned after irradiation for 0, 30, 60, and 100 hrs. and their degree of rancidity was determined.

4) Rheological measurement : (a) The preparative methods for sample employed in this experiment were the same as those described in the previous reports. After addition of 2% (w/v) aluminum stearate to the oil, thorough agitation was maintained for 30 mins., and then the mixture was heated at 130° for 1 hr. to give a completely clear solution. By instantly quenching the hot solution in ice water bath for 1 hr., oil gel was obtained.

The resultant gel was always allowed to stand for 1 hr. in the thermostat prior to all measurements. Throughout the procedure, moisture was avoided as much as possible so as not to affect the system. Measurements were carried out at 25°, employing the concentric cylinder method[1] based on Schwedoff apparatus.

(b) Rheograms of Al-St-oil gel, in the present paper, are represented by the initial rate of deflection (deformation), $d\theta/dt$, in rad./sec. versus the angles $(\theta_0-\theta_G)$ in rad., twisting the top of

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1) H. Matsumura, *et al.* : This Bulletin, **3**, 131(1955).
2) A.M. Trozzolo, E. Lieber : Anal. Chem., **22**, 764(1950).
3) H. Nogami, *et al.* : Yakuzai Buchōkai Nempo, **14**, 85(1954).

** Transmittance of ultraviolet rays through the transparent polyvinyl chloride film was as follows:

Wave length, mμ	380	350	310	300	290
Transmittance, %	76	72	60	35	0

The difference due to the film thickness was negligible.

wire. Elasticity (rigidity), observed on setting of the gel after stirring, was also represented by the ratio of angular twist ($\theta_0-\theta_G$) to the corresponding deflection, θ_G, in rad., of the inner cylinder bob. The values of this ratio were constant over the range of angular twist examined under given conditions, indicating that the larger this value, the larger the rigidity of the sample. Instrumental conditions were as follows: Torsion constant of wire, $K_1=237$, $K_2=58$ dynes/cm.; radius of bob, $R_b=0.54$ cm.; radius of cup, $R_c=0.91$ cm.; height of bob immersed in sample, $h=3.0$ cm.

Experimental Results and Discussions

It is well known that the rancidity of refined oil develops under elevated temperature conditions, especially when exposed to ultraviolet rays in the presence of oxygen. By oxidative rancidification, changes in characteristics of refined peanut oil became more marked with prolongation of irradiation time, as listed in Table I. Iodine number decreased while acid, peroxide, and hydroxylamine values increased, particularly the latter two. In preparing aluminum stearate-oil gel sample for rheological measurements, heating and agitation were always applied to them, so that the effect of the same treatment on rancid oils alone also had to be examined. The results obtained upon heating are also given in Table I, with figures in parentheses, from which it is noted that peroxide and hydroxylamine values were significantly lower, more strikingly in the former, while the acid value was correspondingly increased. On the other hand, the oil stored for 20 days at room temperature without heating after irradiation did not show such variances between acid and peroxide values, as illustrated by the sample III.*

These facts were in agreement with the findings of Toyama and Yamamoto[4] with methyl oleate, of Hizon and Huyck[5] with almond and corn oil, and of Dzens[6]

TABLE I. Constants of Rancid Peanut Oil

Sample No.	Acid value	Sapon. value	Iodine value	Peroxide value	Hydroxylamine value
I	0.8	190	96.4	56.8	7.0
	(1.0)	(182)	(96.6)	(58.0)	(3.4)
II	0.9	204	91.1	343	19
	(2.1)	(185)	(85.8)	(124)	(12)
III	1.7	200	83.1	741	41
	(4.7)	(205)	(80.4)	(97)	(26)
	1.6*	**210**	**78.2**	**712**	**41**
IV	3.0	210	74.8	816	58
	(7.0)	(197)	(76.4)	(106)	(30)

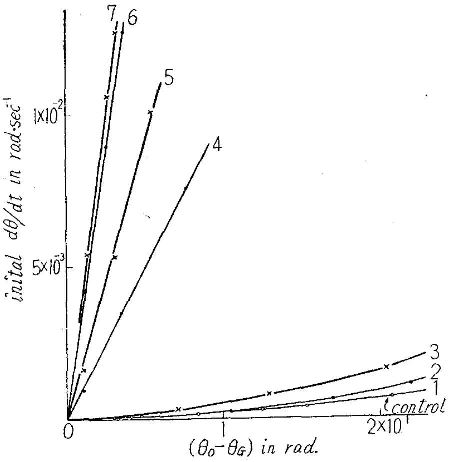

Fig. 1. Initial Rate vs. Angular Twist for Different Rancidity Peanut Oil-Aluminum Stearate Gel (2% w/v) $K_2=58$ dyn. cm.

	Oil Sample	Setting time	$(\theta_0-\theta_G)/\theta_G$
1	I	5, 10 min.	42
2	II	10 (•)	45
3		5 (×)	36
4	III	10 (•)	?
5		5 (×)	
6	IV	10 (•)	
7		5 (×)	

4) S. Toyama, T. Yamamoto: Kogyo Kagaku Zasshi, **55**, 235(1952).
5) R.P. Hizon, C.L. Huyck: J. Am. Pharm. Assoc., **45**, 145(1956).
6) E.G. Dzens: C.A., **33**, 5687(1939).

and other workers. This is explained as being due to secondary reaction in which peroxides produce a variety of other oxidation products such as acids, hydroxy acids, and aldehydes.

A 2% (w/v) Al–St oil gels using these oils of different rancidity were prepared and their rheological behavior was investigated in order to evaluate the effect of oil rancidity on flow properties. The results obtained are shown graphically in Fig. 1. With progress in the degree of oil rancidity, changes in their rheological properties were indicated by the tendency of the initial rate of deformation to increase and finally the rigidity to disappear or to become undistinguishable with 5 and 10 minutes' setting, viz., Al–St gel became increasingly fluid and to lose its gelation property.

Mizuno, *et al.*[7] pointed out that thixotropic gel of Al–St–peanut oil system was much affected by the acid value, its viscosity lowering with increasing acidity of the oil employed, more significantly on heating to above 130° during its preparation. It has been generally known that the presence of a small quantity of free fatty acids, alcohols, and water (being a special case) in Al–St gels makes them fluid, resulting in peptization.[8] This mechanism[9] was supposed to be the bonding of a peptizer to the carboxylate oxygen with the resulting rupture of the polymeric linkage of Al–St rather than preferential coordination with aluminum.

Accordingly, one of the possible explanations of the facts observed in the present investigation might be that a variety of substances produced in oil with rancidification, particularly those which would have increased its acid value act similarly as peptizers to rupture Al–St gel structure and subsequently to render it increasingly fluid. In addition, on gel aging at higher storage temperature as previously reported,[10] it is presumably considered that such effects might be caused partly by similar peptization phenomenon with spontaneous rancidification or deterioration of oil due to the presence of a slight moisture or alumina in the commercial sample.

The question arising from the above experiments is whether there were any relationship between various fixed oils possessing different constants and their rheological behavior when dispensed with Al–St. Similar expriments were carried out with three other oils, and the results obtained are given in Table II and Fig. 2. However, these results do not seem to indicate any definite significance within the present range of investigations.

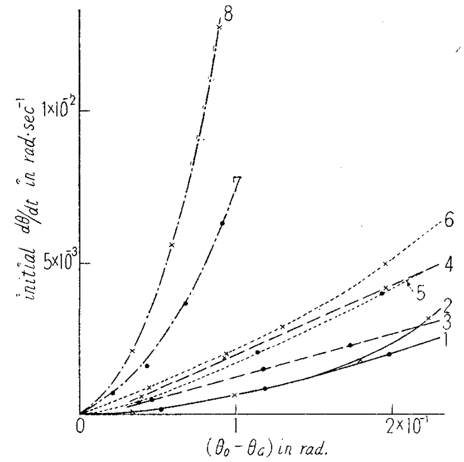

Fig. 2. Initial Rate vs. Angular Twist for Various Oil and Aluminum Stearate Gel (2% w/v) K_1=273 dyne/cm.

	Oil	Setting time (min.)	$(\theta_0-\theta_G)/\theta_G$
1	Peanut	10(•)	11
2		5(×)	9.5
3	Soybean	10(•)	8.1
4		5(×)	6.2
5	Olive	10(•)	8.3
6		5(×)	7.7
7	Linseed	10(•)	3.3
8		5(×)	2.6

7) T. Mizuno, *et al.*: J. Antibiotics (Japan) **4**, 450(1951).
8) A.E. Alexander: J. Oil & Colour Chemists' Assoc., **37**, 378(1954).
9) W.O. Ludke, *et al.*: J. Phys. Chem., **59**, 222(1955).
10) H. Matsumura, *et al.*: This Bulletin, **5**, 21(1957).

TABLE II. Constants of Various Refined Oils

Oil	Acid value	Sapon. value	Iodine value	Peroxide value	Hydroxylamine value	Viscosity* (c. p. s.)
Linseed	0.5	192	185	28.1	0.	72
Soybean	0.06	193	126	33.1	0.9	62
Oilve	1.7	190	84.5	20.6	0.8	68
Peanut	0.8	191	96.4	56.8	7.0	63

* At 25° with capillary viscometer.

These points must be examined further by a larger number of measurements. It must be noted, however, that the deterioration of base oils with rancidification brings about various undesirable effects on the rheological behavior of these oil preparations, as observed in the rancid peanut oil–Al–St system.

The authors wish to express their thanks to Dr. T. Saito, Chief Investigater of Miike Dye Works Research Laboratory (Mitsui Chem. Co.), and to Mr. S. Igata, member of the same Laboratory, for supplying polyvinyl chloride films and determining their ultraviolet transmittance.

Summary

In the colloidal system of aluminum stearate–peanut oil, deterioration of oil by rancidification brought about undesirable effects, causing the flow rate to increase and rigidity to lower in the region of small shearing stress.

(Received October 5, 1957)

UDC 547.792.9.07

14. Kiyoshi Futaki and Senji Tosa: Syntheses of *s*–Triazolidino–[1,2–*a*]–*s*–triazolidine–3,7–dithione Derivatives.

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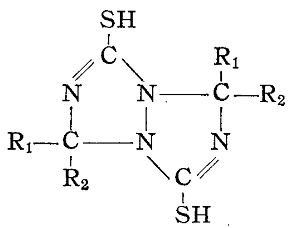
Bailey and McPherson[1] reported the synthesis of 3,5′–dimercapto–5,3′–diphenyl dihydrotriazolotriazole by the reaction of benzalazine with sodium thiocyanate in glacial acetic acid. Later, Sunner[2] studied reactions between hydrazine thiocyanate and aldehydes, and he assumed the chemical structure of the product of this reaction as *s*–triazolino[1,2–*a*]–*s*–triazolines.



In 1953, Miyatake[3] studied the reaction between several azines and sodium thiocyanate according to the procedure of Bailey and McPherson[1] and obtained several compounds which he also assumed as *s*–triazolino[1,2–*a*]–*s*–triazolines.

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1) J.R. Bailey, A.T. McPherson: J. Am. Chem. Soc., **39**, 1322(1917).
2) S. Sunner: Svensk Kem. Tidskr., **64**, 121(1952).
3) K. Miyatake: Yakugaku Zasshi, **73**, 460(1953).