The Sulfur Monochloride Reaction of Fatty Oils

V—Note on the Reaction Velocity and Viscosity of Sulfochlorinated Oils[1]

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Because of the current technical interest in the use of certain sulfur chloride–treated fatty oils for leather-dressing purposes and in the preparation of rust-proofing coatings of the sulfurized varnish type (*3*), it may not be inappropriate now to record data which were obtained some time ago during the course of a critical study of a reaction which for a while bid fair to assume a role as an acceptable analytical procedure (*1*).

The data herein communicated are set down in the order of ascending iodine number of the fatty oils in question. They pertain to fourteen oils, among which are representatives of the drying, the semi-drying, and the non-drying oils, of the fish and marine animal oils, and one liquid wax. These data were obtained, first, by measuring the thermal effect as previously defined (*2*), rather than the exact amount of heat evolved, when 25 grams of dry fatty oil or wax were acted upon by 6.7 per cent of their weight, or 1 cc. of sulfur monochloride (d^{25}, 1.67328; b. p., 138° $C._{760\ mm.}$), and second, by determining the relative viscosity of the oil before and after sulfochlorination. A calorimeter of low radiation loss (*2*) was used in the first series of measurements, an Ostwald viscometer in the second.

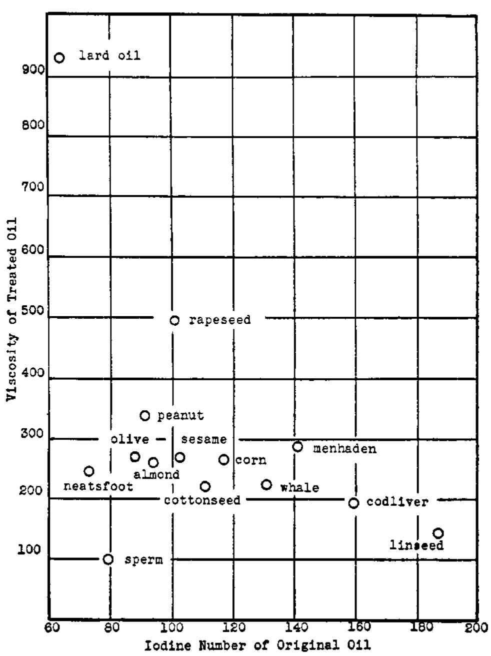

Figure 1—Viscosity of Treated Oil as Function of Iodine Value of Original Oil

It is not the purpose of this communication to attempt an explanation of the anomalies which were found (Table I) to exist in the behavior of the members of this series of fatty oils with sulfur monochloride; such awaits a fuller knowledge of the non-glyceride components of the former than is now extant. Certain deductions from the data, however, appear worthy of comment.

Table I—Thermal Effect and Increase in Relative Viscosity in Sulfochlorination of Fatty Oils

Oil	Iodine No. (Wijs)	Thermal Effect: Max. temp. ° C.	Thermal Effect: Rise per min. ° C.	Relative Viscosity (23°/23° C.): Original oil	Relative Viscosity (23°/23° C.): Treated oil	Evolution of HCl
Lard (oil)	64.1	40.2	5.0	84.0	926.9	Very slight
Neat's-foot	72.9	31.5	3.9	48.3	246.1	Slight
Sperm	78.5	30.3	3.3	24.2	99.9	Abundant
Olive	87.8	26.2	1.0	43.8	268.9	Slight
Peanut	91.2	33.8	2.6	52.2	336.8	Very slight
Almond	94.3	31.3	2.3	42.8	260.6	Slight
Rapeseed	100.7	34.2	3.4	59.4	494.7	Slight
Sesame	103.3	31.5	1.8	39.3	269.2	None
Cottonseed	110.8	27.9	1.0	39.9	217.0	Very slight
Corn	117.0	33.4	1.8	42.5	263.2	Slight
Whale	131.0	33.0	5.5	39.9	218.7	Abundant
Menhaden	142.2	38.6	12.8	45.8	284.5	Abundant
Cod-liver	159.0	33.5	5.6	33.9	192.8	Abundant
Linseed	186.8	36.2	5.2	30.0	138.6	None

The reaction velocity of this reagent and a fatty oil in the incomplete conversion of the latter into a sulfochlorinated product bears no consistent relationship[3] to the degree of unsaturation of that oil. It may be pointed out, for example, that lard and linseed oils, which here typify minimum and maximum iodine numbers, respectively, show approximately the same thermal effect per unit of time and that menhaden oil is unique in its behavior in that the order of its thermal effect is twice that of those oils here grouped with it or, in fact, any other member of the whole series studied.

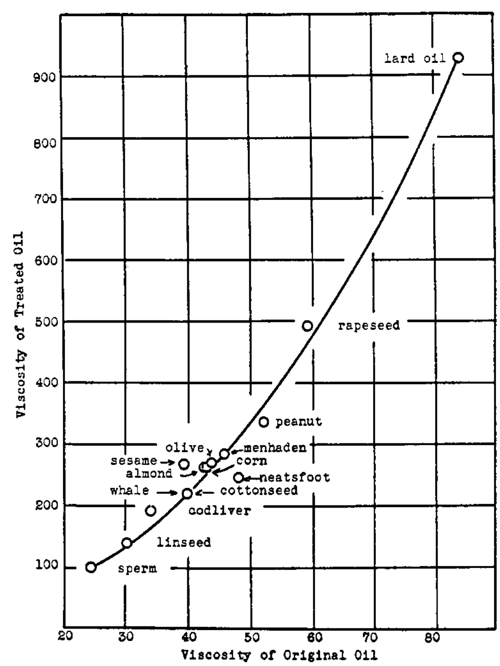

Figure 2—Viscosity of Treated Oil as Function of Original Viscosity

That characteristic of this reaction which makes it impossible to predict with certainty thermal effects from the iodine number is reflected also in the change in viscosity of the parent oil. There likewise appears to be no consistent

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[3] This conclusion is in accord with one made at an earlier date (*2*) when the course of this reaction was studied from the standpoint of the influence exerted upon it by the presence of a diluent.

relationship between the latter and the degree of unsaturation (Figure 1). A few examples will emphasize this fact.

The two oils illustrative of minimum and maximum iodine numbers show an increase in viscosity which is approximately inversely proportional to the "constant" in question. The order of magnitude of change of this property by the non-drying oils, olive, peanut, and almond, appears to be about the same, though peanut oil, which caused the liberation of less hydrogen chloride than the others, forms the most viscous product in this group. Neat's-foot oil forms a product less than one-half as viscous as its associate, lard oil, although its degree of unsaturation is only 8.8 points more. That suggestion of similarity which obtains among the non-drying oils is not apparent in the semi-drying group, for here cottonseed oil forms the product of minimum viscosity whereas that of maximum viscosity, or less fluidity, is formed from sesame oil, where the absence of any detectable quantity of hydrogen chloride during the reaction may have some significance. A better concordance is found among the fish and marine animal group than in the preceding, although menhaden oil, as before, is out of line with the others. In this group an abundant evolution of hydrogen chloride was apparent.

If the oils in this series are arranged in the order of ascending viscosities, and the latter plotted against the viscosities of the treated oil (Figure 2), it will be observed that there has been a concomitant increase in this physical property of the sulfochlorinated product. Sesame and neat's-foot oils are not far enough out of line to affect this generalization.

In the light of the experimental evidence herein disclosed, it appears that the viscosity of the product resulting from the treatment of a fatty oil with approximately 7 per cent of its weight of sulfur monochloride can be predicted more satisfactorily from the original viscosity than from the degree of unsaturation of the parent substance.

Literature Cited

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Relation between Thixotropy and Leveling Characteristics of Paint[1]

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Apparatus is described which makes possible the investigation of the flow properties of plastic systems at exceedingly low shearing stresses of the magnitude involved in the leveling of a paint film.

A method for quantitatively measuring the thixotropic changes in plastic systems is described. It is shown that the yield value of a paint is decreased by mechanical action and increases again after the disturbance ceases. Thus we must distinguish between a temporary or transient yield value that a paint possesses at a definite time after disturbance of the paint and the ultimate yield value that it develops upon long-continued standing.

It is shown that, in addition to surface tension and ultimate yield value, the transient yield value and the thixotropic changes in the paint must also be considered in predicting leveling ability of a paint.

Good leveling is obtained by proper formulation, so that the thixotropic rate of plasticity regain after application of the paint is fast enough to overcome the tendency to sag but slow enough to allow elimination of brush marks before the paint finally sets.

Freundlich (*1*) uses the term "thixotropy" to refer to the reversible gel-sol transformation in which a solid gel is rendered fluid or changed to the sol condition by mechanical action, such as stirring or shaking, and after the mechanical action ceases the sol again reverts to a gel. A paint at shearing stresses below its yield value must be considered a gel, while at shearing stresses above the yield value it must be considered as a sol. Upon removal of the higher shearing stress, the paint again reverts to the gel condition. Hence paints must be considered thixotropic. For the purposes of this discussion any plastic system which is rendered more fluid by mechanical action and regains its former plasticity after the removal of the mechanical disturbance will be considered thixotropic in nature. Paints possessing false body have thus long been recognized as thixotropic, although the term as such has not been applied. It has not been realized, however, that all paints exhibit thixotropic phenomena to a greater or less degree.

Previous Methods of Evaluating Leveling Ability

It is generally recognized that surface tension is the principal force causing leveling of a paint film and that the extent of leveling is governed by the yield value, equilibrium being reached when the shear component of the surface tension is just equal to the yield value of the paint. Waring (*5*) derived the following mathematical expression relating the depth of brush mark (a measure of the leveling) to the surface tension, yield value, and width of the brush mark:

$$h = \frac{d^2 f}{8\gamma}$$

where h = depth of brush mark
d = width of brush mark
f = yield value
γ = surface tension

The author, making reasonable assumptions of surface tension and width of brush marks, calculates that a paint having a yield value of less than 2.8 dynes per sq. cm. would level satisfactorily.

According to this equation, it is only necessary to measure the yield value and surface tension of a paint to predict whether or not it will level satisfactorily. Since in a given class of paints surface tension does not vary greatly, a measurement of yield value alone should suffice. This yield value is not the one commonly obtained by extrapolation of the straight portion of the flow curve to the shearing stress axis, but it is the minimum shearing stress under which the paint will flow—that is, the elastic limit of the paint. The microplastometer (*2*) has been the only instrument which attempted to measure this yield value. This measurement will render an accurate measure of yield value only if the

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