

Thixotropy and rheopexy of propylidone suspensions in arachis oil: effect of median particle size

B. S. CHAWLA

Propylidone oily injection B.P. exhibits thixotropy under high shear rates and rheopexy under low shear rates. The rate and the degree of rheoplectic build-up of structure are influenced by the particle size, the effect increasing as the median particle size is reduced.

A RARE rheological phenomenon has been observed in propylidone oily injection B.P. Although, in common with many suspensions, this preparation exhibits thixotropy or shear thinning at high rates of shear, it shows shear thickening at low rates of shear. This phenomenon is known as rheopexy and has not hitherto been reported in pharmaceutical preparations.

Thixotropy and rheopexy are referred to as non-Newtonian and time-dependent properties. In both cases, the changes in apparent viscosity are thought to be associated with the building or breaking of structure arising from intermolecular forces as well as from interaction between particles.

Thixotropic materials, as characterized by Green & Weltmann (1943, 1944, 1946), Green (1949) and Wilkinson (1960), suffer structural breakdown with a consequent decrease in apparent viscosity when sheared: the degree of breakdown depends on both the duration and the rate of shearing. The rate of breakdown during shearing at any given rate depends on the number of structural linkages that can be broken by the given shearing force. On cessation of shearing, the original structure reforms and the initial apparent viscosity is regained at a rate depending on the availability of possible linkages. During shearing at a constant rate, structural breakdown and reformation proceed simultaneously and a dynamic equilibrium is reached when the internal forces tending to rebuild the structure are equal to the applied shearing forces. The apparent viscosity at equilibrium is dependent on the shear rate.

On the other hand rheoplectic materials exhibit a gradual formation of structure when gently sheared. Freundlich & Juliusburger (1935) were first to observe this phenomenon in thixotropic sols (V_2O_5) of anisometric particles, the time of "solidification" i.e., build-up of structure, being shortened by gentle and regular motion of the sol. It is rare to find both phenomena of thixotropy and rheopexy exhibited by one material. Other materials in which rheopexy has been reported are: gypsum, kaolin and Solnhoten slate (Burger & Sollner, 1936); mixtures of glycerol, water and wheat starch (Bon, 1936); bentonite gels (Hauser & Reed, 1936); clay suspensions (Gurvich, 1956); some polyesters and their concentrated solutions in toluene and ethyl benzene (Steg & Katz, 1965); concentrated suspension of the explosive hexahydro-1,3,5-trinitro-s-triazine (RDX; cyclonite) in molten trinitrotoluene (Williamson, 1959).

From Glaxo Laboratories Ltd., Greenford, Middlesex, England.

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In this paper the effect of particle size on the rheopectic properties of suspensions of propyliodone in arachis oil is reported.

Experimental

APPARATUS

Rheological measurements were made with a Ferranti-Shirley cone-plate viscometer equipped with control unit and X-Y recorder (McKinnell, 1954, 1956, 1960; Van Wazer, Lyons & others, 1963). The apparatus was set up and used in accordance with the instrument manual, an automatic cone-plate setting unit being used throughout the operation, to maintain a constant gap-width between the cone and plate of the instrument.

Two modes of operation were used:

1. To record shearing stress versus rate of shear, the controls were set to give a uniform acceleration of the cone from zero to maximum rate of shear ($1,730 \text{ sec}^{-1}$) in a sweep time of 60 sec and then to decelerate uniformly to zero.

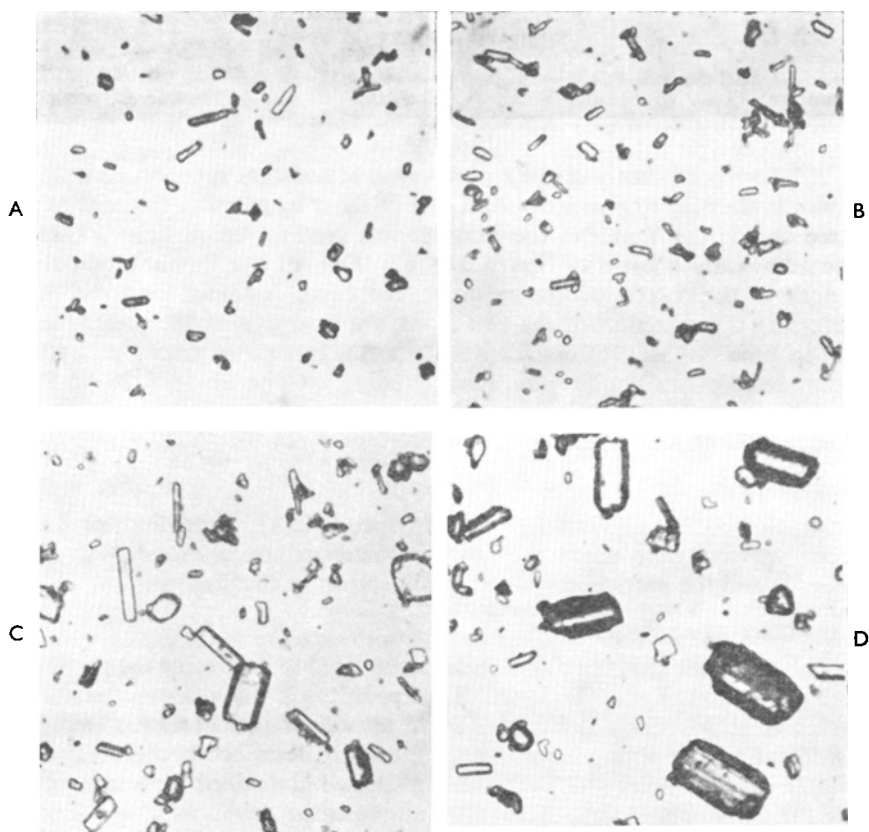


FIG. 1. Crystal shape and size distribution of propyliodone samples A, B, C and D ($\times 285$).

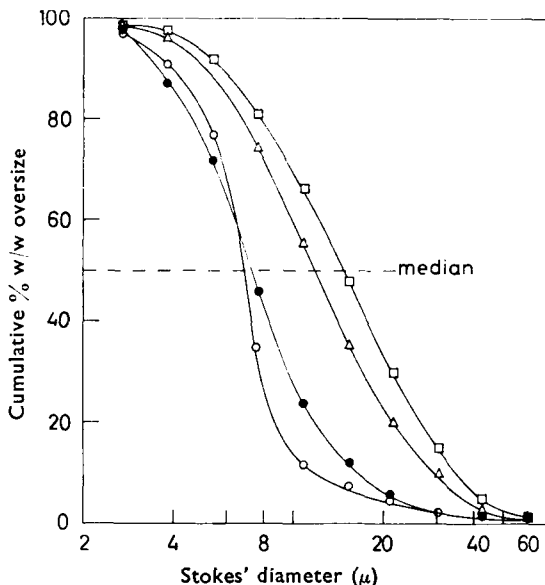


FIG. 2. Particle size analysis of propyliodone crystals. ○ Sample A, median diameter 6.7 μ . ● Sample B, median diameter 7.3 μ . △ Sample C, median diameter 12.0 μ . □ Sample D, median diameter 14.8 μ .

2. To record shearing stress versus time at constant rates of shear, the controls were set to give a constant rate of shear by rotating the cone at a fixed speed; the Y axis of the recorder was used to record time. These recordings are shown in Figs 5 and 6. Due to the limitation in the length of the Y-axis on the recorder, the curve is folded on itself, by reversing the direction of the pen along the time axis at the preselected sweep time (40 sec). Coincidence of the up and down traces indicates attainment of an equilibrium stress reading. Cone angle = 20' 45.5"; cone radius = 3.5 cm; shear stress constant = 24.59; rate of shear constant = 17.30.

MATERIALS

Arachis oil B.P. (Viscosity of 0.74 poise, at 25°.) Propyliodone B.P. Four samples were used: they are characterized by photomicrographs (Fig. 1) and the particle size distribution shown in Fig. 2.

PARTICLE SIZE ANALYSIS

The Sartorius sedimentation balance was used to determine the particle size distribution of propyliodone. The apparatus is an Odén-type balance which gives a continuous record of sediment weight against time. Details of operation and setting up of the apparatus are described by Edmundson (1967). The samples (0.2% w/v) were dispersed in distilled water containing 1.0% w/v polyethylene glycol 600 mono-oleate.

The sedimentation curves were differentiated by an arithmetic method (Stairmand, 1947: British Standards Institution, 1963, Part 2).

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PREPARATION OF SUSPENSIONS

Suspensions of propyl iodone 60% w/v (equivalent to 27.9% v/v) were prepared by gradually adding the powder to arachis oil whilst stirring with a 1 inch diameter three-bladed marine-type propeller, the rate of stirring being regulated to minimize the incorporation of air. When all the powder was dispersed the suspension was stirred for 1 min at 4000 rev/min.

Entrapped air was removed from the suspension at a pressure equivalent to a few mm of Hg till no further air bubbles were visible. Samples were stored in 360 ml wide mouth bottles (internal diameter 6.5 cm) in a horizontal position and after 20 hr the suspensions were stirred gently with a spatula to ensure homogeneity before rheological tests.

RHEOLOGICAL TESTS

Samples for testing on the Ferranti-Shirley viscometer were removed from the bottles with a small scoop and held between the cone and plate (3 min) to reach temperature equilibrium ($25^{\circ} \pm 0.1$). A fresh scoopful was taken for each test and each suspension was tested in the two modes of operation of the viscometer. The resulting flow curves are designated 1 in Fig. 3. The records of shearing stress versus time at constant rate of shear are shown in Fig. 5.

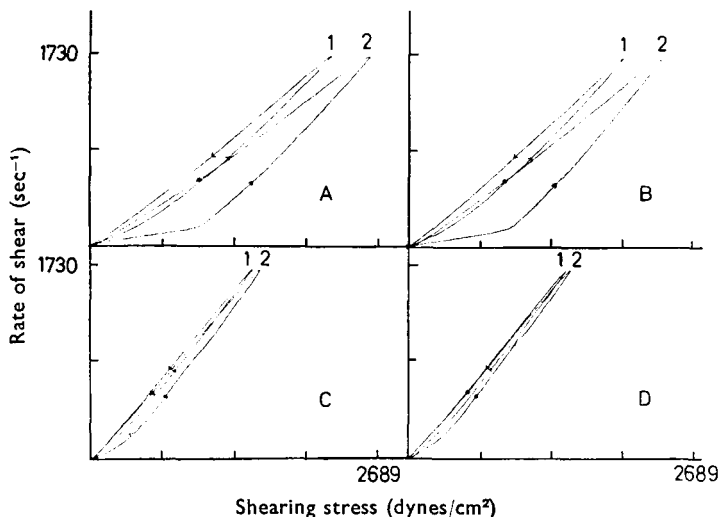


FIG. 3. Flow curves of suspensions A, B, C and D. 1. Before systematic rolling of suspensions. 2. After maximum "rheopeptic" build-up of structure by gentle systematic rolling of suspensions.

The bottles of suspension were then rolled at 18 rev/min with their axes horizontal. Periodically during the rolling, scoopfuls were removed and flow curves were recorded. When the suspensions had attained maximum build-up of structure as shown by the superimposition of consecutive flow curves, the suspensions were tested at a constant rate of shear of 1730 sec^{-1} . The resulting traces are shown in Fig. 5, Series I.

Results

All the suspensions showed similar rheological behaviour, structural build-up when gently rolled, and structural break-down of the system when subjected to a higher rate of shear.

The flow curves of the suspensions determined at various intervals of time of rolling showed an increase in the apparent viscosity and in the degree of thixotropy in the system (judged by the area within the hysteresis loop). Flow curves of the suspensions before rolling and after maximum build-up of structure by rolling are shown in Fig. 3. To illustrate the rheological changes in the suspension during the course of rolling treatment, shearing stress readings versus time of rolling are plotted in Fig. 4. The shearing stress readings were taken from flow curves determined, after various periods of rolling, in the region of rate of shear which showed the widest portion of the hysteresis loop (567 sec^{-1}). In Fig. 4 the graphs show: (a) that the rate and the degree of build-up of structural viscosity increases as the median particle size of the system decreases (graphs with closed symbols); (b) that the degree of thixotropy increases

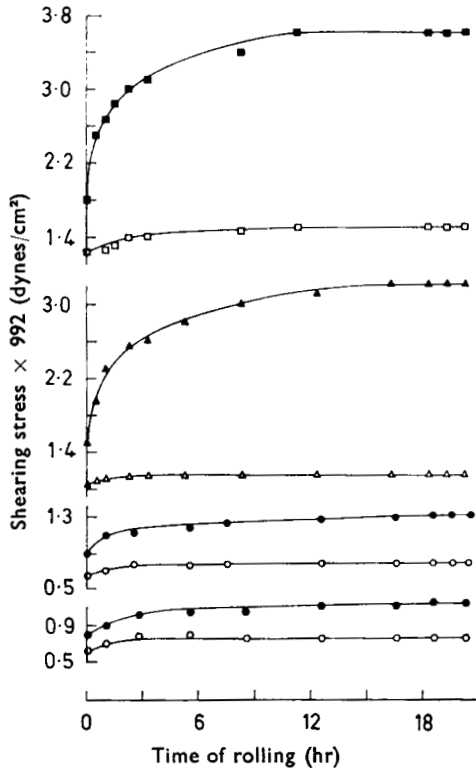


FIG. 4. Demonstrating progressive build-up of "rheopectic" structure with time of rolling. Squares, Susp. A; triangles, Susp. B; circles, Susp. C; hexagons, Susp. D; open symbols, stress reading of the up curve; closed symbols, stress reading of the down curve. Data obtained from flow-curves at 576 sec^{-1} rate of shear.

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as the median particle size of the system decreases, this is indicated by the vertical distance between the up and down curves, characterized by closed and open symbols respectively; (c) that the shearing stress readings of the down curves (open symbols) are higher after rolling.

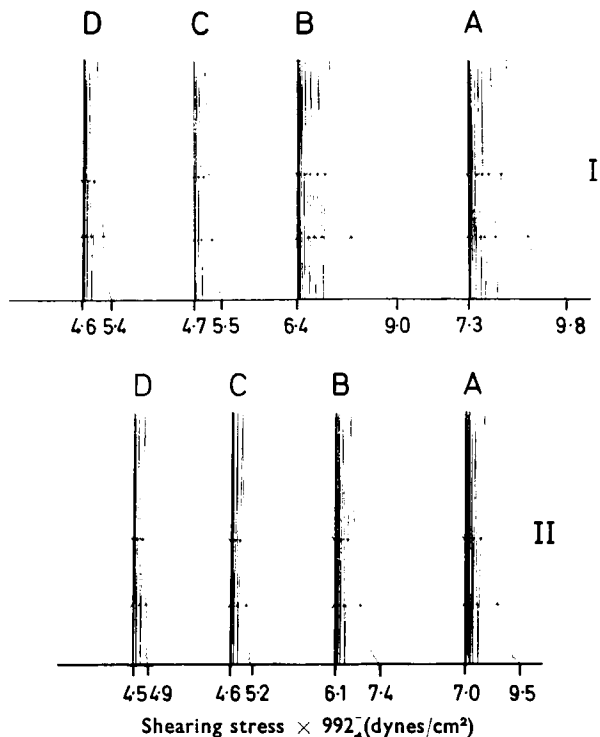


FIG. 5. Plots of shearing stress versus time* at constant rate of shear (1730 sec^{-1}). Series I. After rheopectic build-up of structure by systematic rolling of suspension. Series II. Before rolling of suspension. * One sweep cycle up and down = 80 sec.

The records of shearing stress versus time at 1730 sec^{-1} rate of shear, (Fig. 5, Series I and II) show the strength, the rate of breakdown and the degree of breakdown of structure of the unrolled suspensions and of rolled suspensions; the latter were tested only after maximum build-up of rheopectic structure. The traces show that the structure in the rolled samples breaks down more rapidly under shear than the structure in the unrolled samples, and also that the rate of breakdown is greater with suspensions of smaller median particle size. All suspensions give higher equilibrium stress readings after rolling than before, which suggests that the structure induced by rolling is not only more extensive but also stronger than that existing before rolling.

Although no systematic study of the retention of rheopectic structure has been made, sample A was retested after 4 weeks of storage; the flow curves showed only a slight change in apparent viscosity and thixotropy.

It is difficult to calculate the order of rate of shear that applied in the

rolling experiment. However, the effect of low and high shear rates on structural changes was studied on that suspension which proved most sensitive to shear treatment (Suspension A). This was done by recording shearing stress versus time at various constant rates of shear. Below 104 sec^{-1} rate of shear the system showed structural build-up. The rate and degree of build-up of structure increased rapidly as the shear rate decreased, whereas above 104 sec^{-1} , the rate and the degree of breakdown increased as the rate of shear increased. This is shown in Fig. 6.

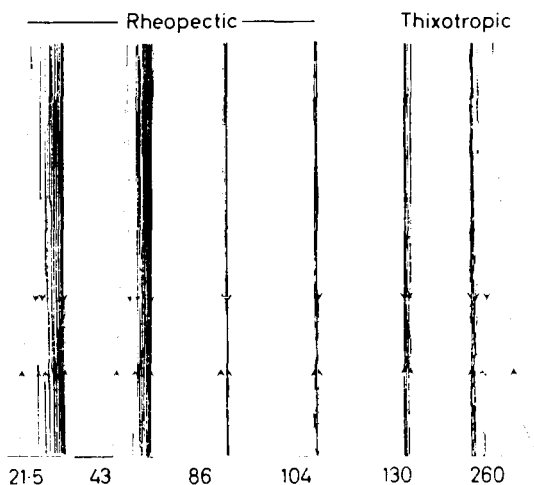


FIG. 6. Demonstrating "rheopectic" and "thixotropic" properties of propylidone suspension in oil (Sample A). Recording of shearing stress (horizontal axis) versus time* (vertical axis) at various constant rates of shear (indicated below each tracing, sec^{-1}). * One up and down cycle = 80 sec.

Discussion

The propylidone suspensions studied here show typical rheopectic properties as defined by Freundlich & Juliusburger (1935).

The terms *rheopecty*, *dilatancy* and *antithixotropy* have sometimes been confused in the literature. Although these phenomena all involve what may be called shear thickening they differ in several respects. Dilatancy is dependent on rate of shear only and occurs when there is a high concentration and close packing of highly dispersed particles; the system dilates under shear, appears dry and stiff, but reverts spontaneously to the more liquid state when the stress is removed. Antithixotropy (Eliassaf, Silberberg & Katchalsky, 1955; Chong, Eriksen & Swintosky, 1960) is dependent on the duration as well as the rate of shear. It is a reversible isothermal increase in consistency during shearing with the system returning spontaneously to a sol state on standing; note that this is the exact reverse of normal thixotropy. Antithixotropic systems are characterized by flow curves that are similar to thixotropic curves but with the direction of the hysteresis loops reversed (Chong & others, 1960; Chawla, 1967).

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With rheopexy, however, the structural build-up and the increase in consistency produced by slow shearing are retained, at least for some time, after shearing ceases. A system with rheopectic structure is in a state of equilibrium.

The influence of median particle size on the rate of build-up, the degree of build-up and the strength of the rheopectic structure has been demonstrated. However, the exact mechanism which causes rheopexy in arachis oil suspensions of propyl iodone is uncertain. According to Freundlich & Juliusburger (1935), an increase in consistency is associated with "orientation of the particles; the regularity of the stirring applied inhibits movements in a vertical axis, and rod-shaped particles are therefore orientated entirely with their axes lying horizontally". Although our propyl iodone crystals were strongly anisometric (Fig. 1), it is difficult to visualize a mechanism whereby such perfect orientation of the particles in the field of shear, would cause an increase in consistency of the suspensions. Our system is relatively simple, propyl iodone crystals in arachis oil, uncomplicated by ionic or hydrogen bond mechanisms. Some form of orientation may take place with propyl iodone crystals under slow shear. The fact that rheopexy is exhibited more readily with smaller median particle size suggests that flocculation or disorientation may be induced by slow rolling.

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