# Investigation of Network Formation in Drying Oils by Dilute Solution Viscometry

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**Dilute solution viscometry was used to monitor the drying of the oils of linseed (*Linum usitatissimum* L.), rubber (*Hevea bransiliensis* [Kunth] Muell. Arg.), soyabean (*Glycine max* (L) Merr) and melon (*Colocynthis* vulgaris Schrad) with a view to gain insight into the mode of network formation prior to the gel point. Intrinsic viscosity values obtained show a rise-and-fall pattern which was attributed to the occurrence of inter- and intramolecular crosslinking. Reduced viscosity values of the solutions of the oils (in both their oxidized and unoxidized forms) show a rise with dilution, indicating the occurrence of major structural changes in the system.**

The use of drying oils in the coatings industry is enormous and as old as the industry itself. Considerable efforts have therefore been made in the past few decades to establish the composition of drying oils and the mechanism of drying, as well as the factors that influence the process. It is now well established that drying oils are characterized by the presence of substantial amounts of such unsaturated fatty acids as linoleic, linolenic and eleostearic acids. The "drying" or, otherwise, the conversion of the liquid oil to a hard film has been proven to be an oxygen-induced cross linking reaction involving the carbon-carbon double bonds in the long chain fatty acid segments of the triglyceride (1,2). A number of factors have also been identified that influence the drying process, namely, temperature, humidity, moisture content, thickness of oil layer, nature of the surface on which the oil is spread, the presence of antioxidants and the nature and quantity of drying accelerators used (3-6).

Techniques that have been used to monitor the development of structure in drying oils include: tack and hardness measurements, gravimetric methods and infrared spectroscopic analysis (7,8). To the author's knowledge, the use of dilute solution viscometry has not been reported. This simple but powerful technique has, in general, been used and rather extensively to study changes in size and structure in polymeric systems via the measurement of intrinsic viscosity which is a measure of the hydrodynamic volume (or size) of a molecule (9). Indeed, any structural changes in a polymeric system which result in significant changes in its size are known to cause dramatic changes in intrinsic viscosity. Examples are: branching in a polymer decreases its solution viscosity at constant molar mass (10); ionization of a weak polyelectrolyte with dilution has been reported to cause an increase in the solution viscosity as a result of chain expansion induced by coulombic repulsion (11). Similarly, the formation of a liquid crystalline phase in a solution is accompanied by a change in viscosity as a result of structural changes in the system as it goes from a disordered (isotropic) to an ordered (anisotropic) phase and vice versa (12).

It therefore seems possible to monitor the structural changes in a polymerizing (drying) oil by dilute solution viscometry. This work is a preliminary attempt to do that and the objective is to gain insight into the mode of network (film) formation prior to the gel point in drying oils and related crosslinking systems used in the coatings industry.

## EXPERIMENTAL

*Materials.* The oils of rubber (*Hevea bransiliensis* [Kunth] Muell. Arg.), soyabean (*Glycine max* (L) Merr) and melon (*Colocynthis vulgaris* Schrad) seeds were solvent-extracted in our laboratory. The oils were bleached with fuller's earth. Rubber and melon seed oils were alkali—refined using Cocks and Rede's method (13) to acid numbers of 0.94 and 0.14, respectively. The soybean oil was not alkali-refined as its acid number of 0.18 was considered low enough. The linseed oil (*Linum usitatissinum* L.) with acid number 0.7 was obtained in a refined state as a gift from Damex Paint Industry, Oji-River, Anambra State. The oils have the following iodine numbers: linseed (180), rubber (142), soybean (130) and melon (115).

Lead and cobalt naphthenates (driers) used in this work were obtained from Ebony Paints (Nigeria) Ltd, Enugu, Anambra State; and they contain 35.5% Pb and 6.81% Co, respectively.

*Equipment.* A viscosity bath; an Oswald-Fenske viscometer (type A 52), glass plates (23 cm × 7.5 cm).

*Preparation and casting of oil-drier mixtures.* A weighed amount of each oil was mixed with the required amount of the metal naphthanate to give a drier level of 0.50% (Pb) and 0.05% (Co) in the mixture. The glass plates for film casting were prepared by taping off an area of about 23 cm × 5 cm using a monolayer of a paper tape of thickness 0.01 mm. Each oil-drier mixture was gently poured on the taped-off area on the glass plate and then leveled with a doctor's blade to give a wet-film thickness of 0.01 mm. The coated plates were left to dry under a room temperature of 32°C.

*Monitoring the drying process by viscosity measurement.* The drying of the oil film was monitored at two-hour intervals for a total period of 12 hr for rubber, melon and linseed oils and 10 hr for soyabean oil. At each time interval, a known weight of the drying oil film was removed and dissolved in the solvent (toluene) and then diluted to the following concentrations: 0.170, 0.345, 0.520, 0.690 and 0.860 g per deciliter. Each dilute solution was filtered using a sintered glass funnel and its efflux time was obtained using an Oswald-Fenske viscometer (type A 52) in a viscosity bath equilibrated at 30°C. Three efflux time readings which agreed to within 0.20 seconds were obtained for each solution. The solvent efflux time was 172.60 seconds.

It should be noted that from about the 10th hour the oil film dissolved with difficulty as the system approached the gel point; consequently, viscosity measurements were not made beyond the 12th hour.

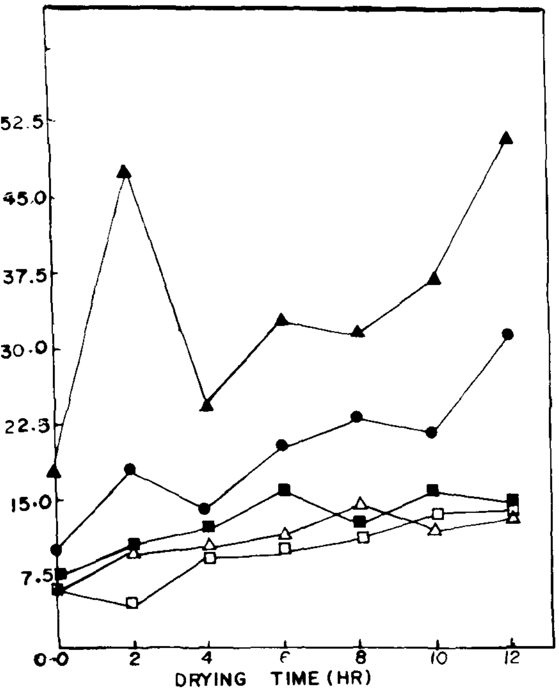

**FIG. 1. Reduced viscosity versus drying time for linseed oil: (▲), 0.17; (●), 0.345; (■), 0.52; (△), 0.69; (□), 0.86 g/dl.**

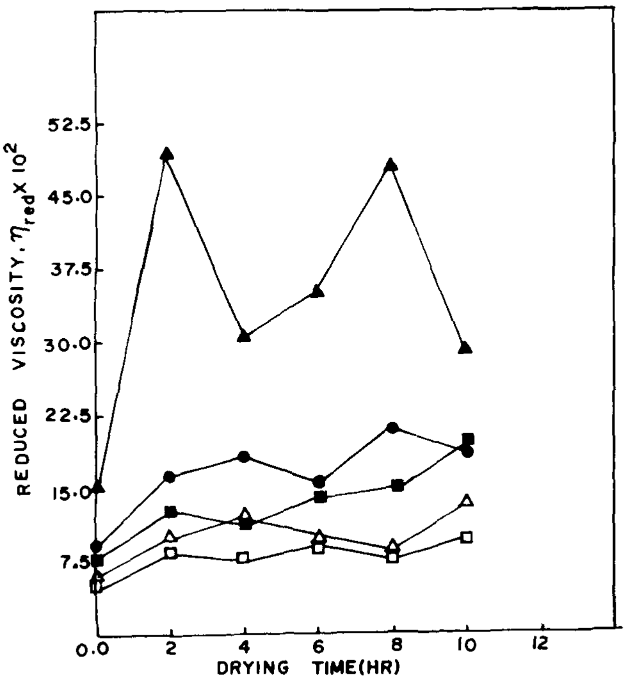

**FIG. 3. Reduced viscosity versus drying time for soybean oil: (▲), 0.17; (●), 0.345; (■), 0.52; (△), 0.69; (□), 0.86 g/dl.**

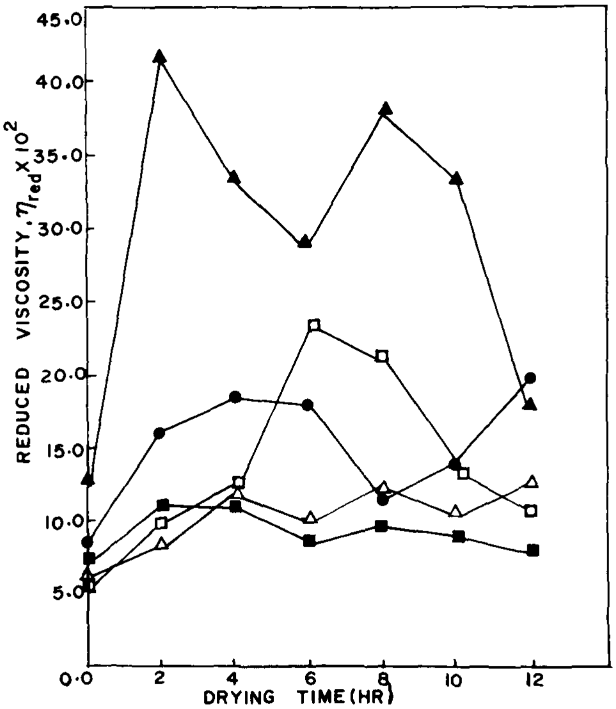

**FIG. 2. Reduced viscosity versus drying time for rubber seed oil: (▲), 0.17; (●), 0.345; (■), 0.52; (△), 0.69; (□), 0.86 g/dl.**

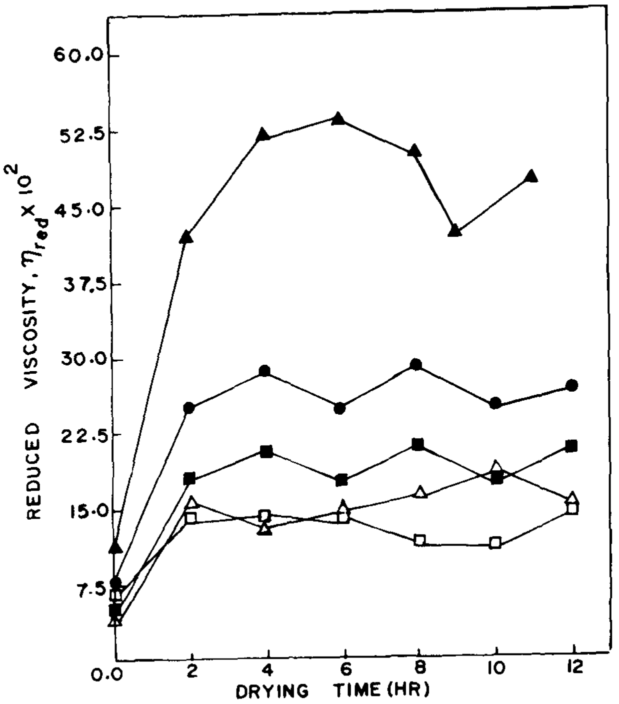

**FIG. 4. Reduced viscosity versus drying time for melon seed oil: (▲), 0.17; (●), 0.345; (■), 0.52; (△), 0.69; (□), 0.86 g/dl.**

*Results.* Values of reduced viscosity ($\eta_{red}$) were obtained from the efflux times using the expression:

$$\eta_{red} = (\eta_{sp}/C) = (t - t_s)/t_s.C \qquad (1)$$

where $\eta_{sp}$ is the specific viscosity; t and $t_s$ are the efflux times of the oil (oxidized or unoxidized) and toluene, respectively; and C is the concentration of the solution in g per deciliter. Plots of reduced viscosity versus drying time in hours are given in Figure 1 (linseed oil), Figure 2 (rubber seed oil), Figure 3 (soybean oil) and Figure 4 (melon seed oil). Each figure contains a set of five curves

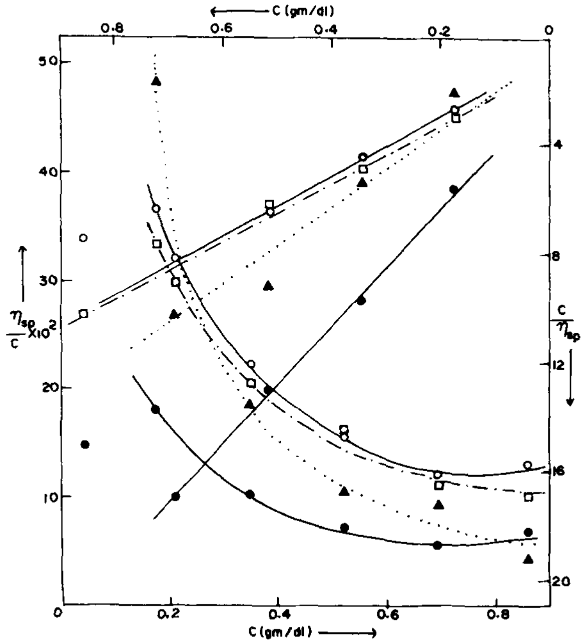

**FIG. 5. Reduced viscosity and its reciprocal versus concentration for linseed oil at varying drying time (hr): (●), 0; (▲), 2; (□), 6; (○), 10.**

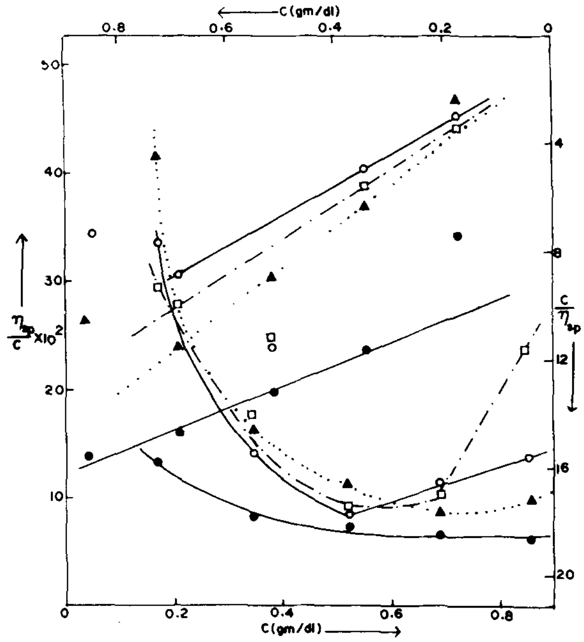

**FIG. 6. Reduced viscosity and its reciprocal versus concentration for rubber oil at varying drying time (hr): (●), 0; (▲), 2; (□), 6; (○), 10.**

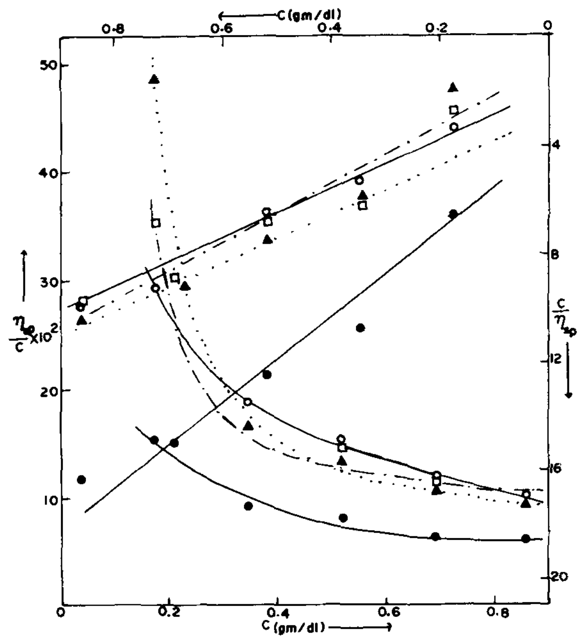

**FIG. 7. Reduced viscosity and its reciprocal versus concentration for soybean oil at varying drying time (hr): (●), 0; (▲), 2; (□), 6; (○), 10.**

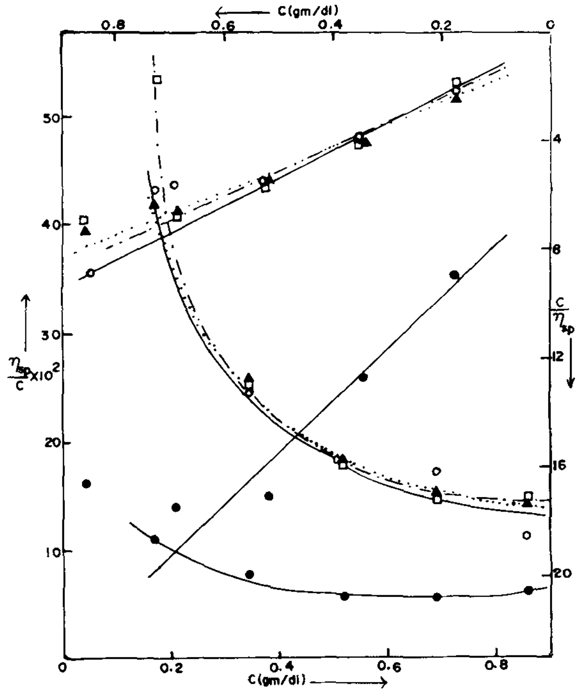

**FIG. 8. Reduced viscosity and its reciprocal versus concentration for melon seed oil at varying drying time (hr): (●), 0; (▲), 2; (□), 6; (○), 10.**

obtained at five different concentratins: 0.170, 0.345, 0.520, 0.690 and 0.860 g/dl. Three significant observations are evident from each of the above figures: first, there is an initial rise in reduced viscosity, followed by a rise-and-fall pattern as the drying progressed to the 10th or 12th hour; second, there is an enhancement of reduced viscosity with dilution; third, the overall shape of each reduced viscosity versus drying time curve tends to change with dilution, particularly at extreme concentrations.

This unusual dilution effect on the viscosity of the drying (oxidized) oil, as well as that of the pure (unoxidized) oil, is further illustrated graphically for the four oils in Figures 5 to 8, in which reduced viscosity ($\eta_{sp}/C$) is plotted against C (g/dl) on the left and bottom ordinates.

Similar plots were obtained at the 4th and 8th hours but were not included in order to decongest the figures. The above behavior deviates from the normally observed rise in reduced viscosity as the concentration of a macromolecular system is increased. It was therefore not possible to fit the viscosity data here with such empirical expressions as the Huggins and Kraemer equations. Instead, a new expression (equation (2)) was used.

$$\eta_{sp}/C = [\eta]/(1 + BC) \qquad (2)$$

the reciprocal of which is

$$C/\eta_{sp} = 1/[\eta] + B.C/[\eta] \qquad (3)$$

where B is a drying-time dependent factor and $[\eta]$ is the intrinsic viscosity. Thus, using equation (3), plots of the reciprocal of reduced viscosity versus concentration were carried out on the right and top ordinates of Figures 5-8. In general, the plots appear linear with a few deviating points, which occur mainly at low and high concentrations. Again, similar linear plots were obtained with the viscosity data at the 4th and 8th hours.

Intrinsic viscosity values, given in Table 1, were obtained by taking the reciprocal of the intercepts at C = 0. Plots of intrinsic viscosity versus drying time are given in Figure 9; again, a rise-and-fall pattern is observed as in the case of reduced viscosity. Values of the factor B, given

**TABLE 1**

**Intrinsic Viscosity Values of Oil-Drier Mixtures in Toluene at 30°C**

| Age of cast film (drying time), hr | Oil | | | |
|---|---|---|---|---|
| | Linseed | Rubber | Soybean | Melon |
| 0 | 0.50 | 0.110 | 0.25 | 0.17 |
| 2 | 1.33 | 0.91 | 0.33 | 0.91 |
| 4 | 0.33 | 1.11 | 0.83 | 3.33 |
| 6 | 0.91 | 0.83 | 0.91 | 2.50 |
| 8 | 0.59 | 1.43 | 1.25 | 5.00 |
| 10 | 1.43 | 0.91 | 0.50 | 3.33 |

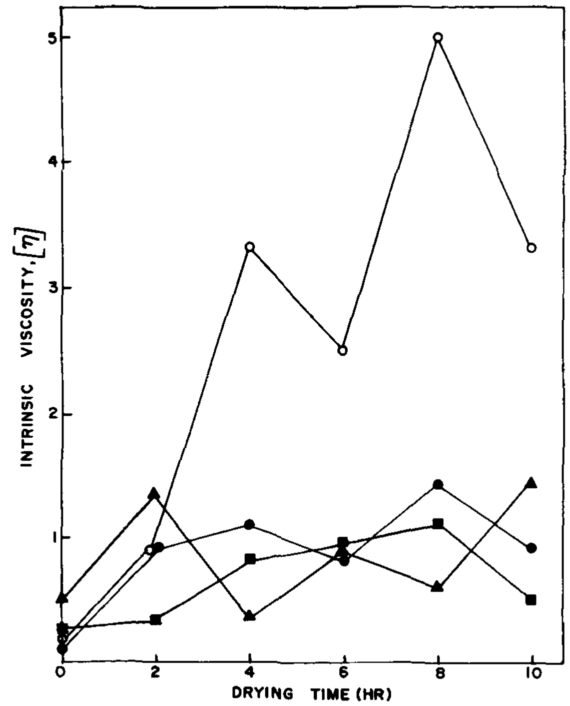

FIG. 9. Intrinsic viscosity versus drying time for the various oils: (▲), linseed; (●), rubber; (■), Soyabean; (O), melon.

**TABLE 2**

**Values of The Factor B at Various Stages of Drying**

| Age of cast film (drying time), hr | Oil | | | |
|---|---|---|---|---|
| | Linseed | Rubber | Soybean | Melon |
| 0 | 12.28 | 0.90 | 4.00 | 3.19 |
| 2 | 18.33 | 13.80 | 3.22 | 7.34 |
| 4 | 3.39 | 14.69 | 10.28 | 26.01 |
| 6 | 9.88 | 10.46 | 9.72 | 21.18 |
| 8 | 4.91 | 14.89 | 21.31 | 45.25 |
| 10 | 16.91 | 10.60 | 4.52 | 33.00 |

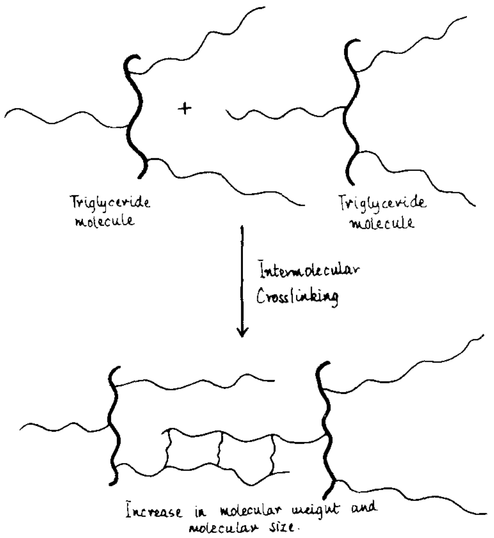

FIG. 10. Schematic of network formation in Drying Oils via intermolecular crosslinking reaction.

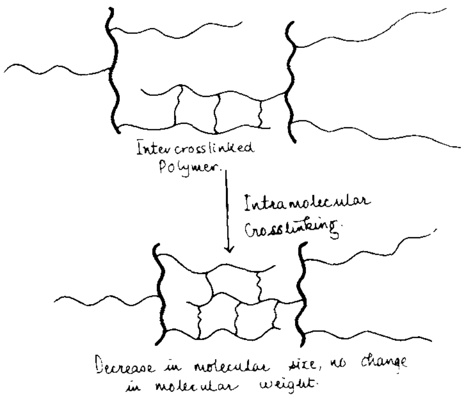

FIG. 11. Schematic of network formation in Drying Oils via intramolecular crosslinking reaction.

in Table 2, were obtained by multiplying the slopes of the linear curves by their respective intrinsic viscosity values. B is seen to vary in the same manner as the intrinsic viscosity.

## DISCUSSION

The observed rise-and-fall pattern in both reduced and intrinsic viscosities of a drying oil system may be rationalized by considering the occurrence of two competing processes: intermolecular crosslinking or polymerization leading to increase in molecular mass and size (Figure 10) and intramolecular crosslinking which leads to decrease in size and no change in molecular mass (Figure 11). The former is expected to lead to the observed rise while the latter accounts for the observed fall. Intermolecular crosslinking appears more favored during the early stages of the drying as can be seen from Figures 1 to 4 and 9; while intramolecular crosslinking becomes more probable at the advanced stages of the drying process, by which time the drying oil molecule shall have acquired several unsaturated fatty acid segments.

The involvement of intramolecular crosslinking appears supported by the drying behavior of the more unsaturated oils: linseed and rubber, both of which show marked rise-and-fall patterns (Fig. 9). This behavior can be attributed to the availability of more unsaturated bonds on their fatty acid segments which can readily be involved in intramolecular crosslinking. Melon seed oil, on the other hand, being the least unsaturated, shows almost a continuous and spectacular rise in intrinsic viscosity, indicating the predominance of intermolecular crosslinking.

Also, linseed and rubber seed oils exhibit much harder films on drying than soybean and melon seed oils probably as a result of their greater ability to undergo more of intramolecular crosslinking than intermolecular crosslinking. In other words, intramolecular crosslinking appears to be largely responsible for the hardening of an oil film.

The observed rise in reduced viscosity with dilution in all the samples (including the unoxidised oil) implies that the hydrodynamic volume (hence the molecular size) of the system undergoes expansion as the solution becomes more dilute. This behavior is similar to that observed in systems that exhibit liquid crystalline structure (12). In such liquid systems, the molecules in the ordered regions would tend to move apart on dilution; this would result in increase in their hydrodynamic volumes and hence a rise in the solution viscosity. On a similar note, the amphipatic nature of the drying oils—consisting of the polar ester groups and the nonpolar fatty acid chains, may lead to the formation of "molecular clusters" or "ordered structures" which would tend to disperse on dilution. Thus, the observed enhancement of reduced viscosity with dilution (Figures 5 to 8) appears to support the existence of such clusters; and, as they disperse with dilution, the hydrodynamic volume of each molecule would be expected to increase and hence the observed rise in viscosity. The change in shape of the reduced viscosity versus drying time curve with dilution (Figures 1 to 4) also lends support to the occurrence of structural changes in the system.

It should be noted that the observed fluctuations in reduced and intrinsic viscosities with drying time cannot be attributed to "sol effect" (9) because the crosslinking oil films had not reached the gel point as evidenced by their complete solubility in the solvent used.

Finally, the consonance in the variation of the factor B and intrinsic viscosity appears to indicate that B may be a measure of the hydrodynamic volume of the crosslinking oil; this observation, however, needs further investigation.

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