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VISCOSITY BREAKDOWN
OF OILS

by H. A. Pohl

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BuShips P. O. No. 1666/42 of 28 October 1941; BuOrd Conf. P. O. No. 2609
of 3 January 1942; and BuAero Project Order No. 115/43 of 13 July 1942.

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ABSTRACT

An analysis of the causes of the instability of the viscosity characteristics of oils is presented. Correlations are made between the structure of the molecules and the tendency of the oils to break down. It is demonstrated that the larger molecules present in oil can be torn apart by the violent motions which they experience in modern machinery.

From fundamental considerations, predictions can be made on the stability of the large molecules which are used as oil additives, and of their breakdown by certain types of machinery. This knowledge should enable more intelligent choice to be made in compounding oils than before, and reduce dependence on trial and error.

VISCOSITY BREAKDOWN OF OILS

- I. AUTHORIZATION: Bureau of Ships Project Order No. 1666/42 of 28 October 1941.
- Bureau of Ordnance Confidential Project Order No. 2609 of 3 January 1942
- Bureau of Aeronautics Project Order No. 115/43 of 13 July 1942

II. STATEMENT OF PROBLEM:

1. The purpose of this work is to present a brief account of contemporary knowledge of the phenomenon of viscosity breakdown in polymer blended oils and to contribute to an understanding of the causes of such breakdown.

III. PURPOSE OF THIS WORK:

2. Modern lubricants and hydraulic oils generally contain additives. Certain additives such as long chain polymers possess important characteristics. First, they have the very desirable property of flattening out the viscosity-temperature curve, or increasing the viscosity index of an oil. Second, the addition of a small percent of the polymer increases the viscosity of the oil greatly.

3. This improvement of the quality of an oil may allow the use of the same oil at all seasons, hot or cold; may impart improved performance; and may permit the use of otherwise unusable oils, e. g., halocarbons, which have valuable properties such as low inflammability.

4. Despite these valuable properties these polymer blended oils are subject to an as yet unpredictable permanent loss in viscosity which may be of considerable magnitude 1, 2, 3, 4, 5, (50% loss in viscosity measured at 100°F). Side by side with this viscosity loss occurs an unfavorable drop in the viscosity index. This uncertainty in the behavior of given polymer blended oils under service conditions often causes a natural hesitation in using them. Until this uncertainty is dissipated, polymer blended oils cannot be used with confidence except in limited applications. However, for many uses as in the case of hydraulic oils or recoil oils, a slight viscosity breakdown is not important.

5. Little seems to be generally known of the factors causing viscosity breakdown except in a qualitative sense. The methods for going about minimizing it or preventing it are handicapped by this. It is the aid of this report to present the facts important for an understanding of the causes of breakdown due to high mechanical shear, and to present a clear useful picture of the phenomenon. With these one may proceed to attack the problem of minimizing mechanical breakdown of oils in service.

IV. KNOWN FACTS BEARING ON THE PROBLEM

6. Viscosity breakdown is particularly to be noticed where oil experiences high shear, high temperature, or both. Certain types and designs of equipment seem to promote breakdown. Before entering into a discussion of the precise processes and conditions under which viscosity breakdown occurs, it may be well to present a simple picture of the nature of polymers, polymer additives, oils, and of the proposed mechanism of breakdown. A polymer is a compound whose molecules are comprised of a series of basic molecular units or submolecules [e.g., $(-CH_2-)$ or $(-CHR-CH_2-* \text{ or } -R-)$] * held together by primary valences. The number of submolecules in each polymer is termed the degree of polymerization. The chains so formed may be branched or cross-linked, though for the polymers in use as additives, one finds only relatively unbranched and non-cross-linked molecules. These "straight chain" or "linear" molecules are not usually extended in a straight line but are considerably coiled and kinked. (See Plate II). They are rather easily pushed into different shapes, depending on external and internal forces. The molecular weight of a particular polymer is proportional to the number of monomeric units or "sub-molecules" as they are called.

7. The original oil base stocks also consist of complex molecules but they are usually of relatively low molecular weight and chain length, often including cyclic and branched sections and therefore are small as compared to the high polymer additives.**

8. It is important that polymer molecules be thought of as fundamentally the same as all other molecules in chemical and physical aspects and possessing only one important difference - size. They are large ponderous chains of atoms which are relatively slow-moving. Their internal links may more easily be pulled apart by distributed external mechanical forces. This is because of the great pull exerted by the sum of all the chain members when a small force is exerted at each point over the entire chain. The shorter the molecule, the less likely the bonds are to be broken by such distributed external forces.

9. In any one sample of crude synthetic polymers used as oil additives, there are usually species of widely varying molecular weight. This crude polymer is said to be "inhomogeneous" as regard to molecular weight. It is common

*NOTE: The end groups will generally differ from those within the polymer but they are relatively few in number.

**NOTE: The molecular weights of the polymer additives usually exceed 5000 while most blended oil base stocks average about 200 in molecular weight.

practice to specify an average molecular weight in referring to a polymer and this is usually that average molecular weight as determined from the viscosity in dilute solution. ("weight average" molecular weight⁹).

10. From this picture of the nature of polymer blended oils and their breakdown, one may proceed to examine current knowledge of the phenomenon. The viscosity degradation of polymer blended lubricants is generally believed to be due mainly to the breaking down of the long chain polymer additives under the conditions of use. There are several reasons for suspecting the additives as the cause.

(a) The viscosity of oils not containing polymers usually increases slightly rather than decreases with use. This increase is probably due to the slow oxidation and polymerization of certain fractions which are part of most lubricants.

(b) The viscosity of polymer blended oils is very sensitive to the M.W. of the polymer, decreasing with M.W.

(c) The molecular weight of the polymer is found to be considerably decreased following the mechanical action. (See Table II and paragraph on "Milling" below.)

(d) The degradation of long chain polymers is known to occur upon milling even in the pure state.

(e) The use of a mechanically pre-stabilized polymer reduces viscosity breakdown considerably. (See paragraph 18).

11. It may safely be assumed that the breakdown of the polymer is the basic cause of the viscosity breakdown of the polymer blended oil and therefore any information concerning the breakdown of polymers in general will be of value in understanding the phenomenon.

12. It is interesting to note at this point that one must qualify the term "viscosity breakdown". Concomitant with the polymer breakdown there generally exists a viscosity lowering at temperatures around 100°F to 210°F. However, the viscosity index of the polymer blended oil is also observed to drop with use. This means that at lower temperatures the viscosity of the oil may even increase due to the process of shear breakdown. If the tests are run at low temperatures, the viscosity may decrease, remain sensibly constant, or even rise during the run.

The last instance would tend to further increase breakdown. This peculiar action occurs because of the anomalous behavior of viscous mixtures near the gelation point. It will consequently be necessary to specify the temperature at which the viscosity changes are caused, and at which they are to be compared.

13. Polymers may be degraded by many means. (1) Mechanical (including milling, shaking, supersonics, shear), (2) Thermal, (3) Chemical, (4) Electrical, (5) Photolytic. Only mechanical means, however, will be considered in detail in this discussion.

Breakdown by Mechanical Means

A. Milling.

14. It has been demonstrated that by milling, kneading, grinding, or otherwise working the pure polymer or its solution, it may be "degraded" or given a lower degree of polymerization 2, 6, 7, 8, 10, 11, 17. Occasionally, an oxidizing agent is added to accelerate the process¹⁰. Starting with material of high molecular weight under fixed conditions there exists a lower limiting molecular weight which on continuance of the treatment exhibits no further change 1, 2, 6, 7. As an example, polystyrene polymers of original molecular weights of 600,000 or 100,000 both dropped to a constant lower limit of 12,500 after 12 hours grinding in a ball mill with water as coolant. It is apparently possible to reduce the rate of such degradation by the addition of a stabilizer.¹¹

B. Shaking.

15. Violent shaking of solutions of polymers also results in a lowering of the molecular weight.¹¹ The exclusion of most of the atmospheric oxygen seems to have a small order effect in reducing the amount of degradation.

C. Ultra-sonics.

16. The investigation of the effects of ultrasonic energy in the form of compressional (or longitudinal) waves on solutions of high polymers has been intensively studied 12, 13, 14, 15, 16 and the factors involved are well understood. Space does not permit a detailed presentation of the results except the mention of the following points important to an understanding of shear breakdown.

- (1) Polymers of any higher molecular weight are always

reduced to a common lower limiting molecular weight under identical conditions of exposure. Beyond this lower limit no further breakdown will occur.

(2) The rate of breakdown is greater on longer molecules; also greater on linear than on coiled or branched chains.

(3) Breakdown is complete in a few minutes.

(4) The rate is appreciable only in solutions where a "gel" structure is present (concentration is high enough to cause chains to interlock)

(5) This point and point (2) is reflected in the equation which obtains for the breakdown rate:

$$\frac{dx}{dt} = k (\beta - \beta_{\infty})$$

where x = no. of molecules broken
t = time
k = constant

β, β_{∞} are degrees of polymerization at any instant and at infinite time respectively.

(6) Increase of viscosity of the solvent increases the degree of degradation.

(7) Rate of degradation is proportional to the frequency and highest if the frequency is varying.

(8) Pressure on the system decreases the rate and degree of degradation.

(9) Polymerization or depolymerization can be accelerated by supersonics but equilibrium cannot be shifted.

(10) The theory is rather well developed and successful in its application. It is based on the picture of "breaking strains" developed by the small solvent molecules rushing through the network of relatively immobile large chain-like polymer molecules. The motion is caused by the impact of the sound waves. Comparison of this picture with that envisioned for shear breakdown will be made later. (Par 45, 46.)

It can be seen that ultrasonics furnishes a means of rapidly reducing the molecular weight to a desired maximum. This can

find application in the stabilization and the testing of the stability of polymer additives for oils. Conclusions can also be drawn as to the structure and degree of branching, etc. of a given polymer oil.

D. Shear

17. Breakdown by shear of the polymer blended oils is a subject of considerable interest. It has been observed and investigated by a number of workers. Various factors affecting its occurrence have been found 1, 2, 3, 4, 5, 6, 7. So far, the lack of a precise study of the phenomenon has prevented discovery of the exact relationship of the various known factors. The mechanism and behavior of polymer breakdown is consequently little understood.

18. Investigators have used colloid mills, gear pumps, piston pumps, truck transmission gears, capillaries and orifices to produce viscosity breakdown. The following facts have been found:

(1) Shear breakdown occurs more rapidly with higher molecular weight polymers.

(2) There exists a minimum molecular weight to which higher polymers are broken down under a given set of conditions.

(3) Little breakdown is experienced except at high shear rates. Precise information is lacking.

Turbulence of flow and anomalous viscosity have been unknown variables in most experiments to date.

(4) Viscosity, temperature and concentration 1,2,3 play roles, but how is not well known.

(5) It is reported that the blending of two polymers to make a polymer additive for oils has revealed an increased stability against shear breakdown 3, p.67. For example, a mixture of acryloids and polybutene is more stable than the same % by weight of either alone in oil.

(6) There is considerable discussion in recent reports 1, 2, 3, 4, 5 as to which type of apparatus should be used to test shear breakdown. This is because the type and amount of breakdown is dependent on the conditions of breakdown. The presence of valves, capillaries, gears, and points of high friction and temperature in varying extent will cause many different combinations of breakdown type.

(7) The distribution of molecular weights in a given polymer batch before and after breakdown is of considerable importance but has not been carefully investigated nor adequately observed during most experiments. In accordance with (1) (Par. 18) the high molecular weight fractions of the mixture break down most rapidly. This tends to cut short the molecular weight vs. frequency curve at medium molecular weights after shear breakdown. The use of a polymer of initially homogenized molecular weight has been shown to greatly decrease the viscosity breakdown^{1,2} of the resultant polymer blended oil if it is compared with an oil of identical viscosity but made with crude polymer. (by "crude" is meant one as usually obtained, consisting of a mixture of polymers of widely different molecular weight). This phase of polymer preparation for oil blending deserved considerable attention.

(8) Polymers of different chemical nature appear to vary in susceptibility to shear breakdown^{3,4,7}. Much more cannot be stated definitely because very little control of molecular weight, homogeneity, etc. was taken.

(9) The effect of the chemically reactive impurities and of added agents has not been greatly studied. Of particular interest is the observation that the addition to the solution of an unnamed stabilizer to the extent of 1% serves to minimize breakdown during the kneading of polybutene 11. A fertile field for investigation may lie in the direction of finding other stabilizers for shear breakdown.

(10) Various means of minimizing viscosity loss due to shear have been employed, using the principle of pre-stabilization. Here polymers are treated before blending so as to reduce their susceptibility to breakdown. Mechanical action,^{1,2} heat treatment,^{5g} and also purification by fractionation² to obtain more uniform molecular weights have been used.

WORK OF THIS LABORATORY

19. Because the problem of the breakdown of polymer blended oils by shear is of considerable practical importance in connection with research for the best lubricants, hydraulic oils, and recoil oils, and because that problem is far from solved by the use of empirical test methods, it is timely to undertake a fundamental search for the why and how of such breakdown. The following discussion is an attempt in this direction.

20. From the facts assembled so far, three concepts can be pictured for the process of polymer breakdown during use in machines. First, the shearing stress in the liquid is regarded simply as a means of producing tensile strain in the polymer bonds. These, aided by the usual thermal motions of the molecules, are sufficient to cause cleavage. Second, the picture is regarded as similar except that chemical impurities act to aid breakdown of the already strained bond. Third, boundary effects such as occur at wall interfaces are important. Here local temperature effects on the walls at points of high friction and intense mechanical mashing are regarded as responsible for depolymerization, i.e. thermal and mechanical breakdown. Probably all play a role in an actual hydraulic or other machine.*

THE ONSET OF BREAKDOWN

21. Any proposed mechanism must include a means of producing strains and tensions on the primary valence bonds which hold the huge polymer molecules together. These bonds would at first though appear to be too strong to break under conditions of flow in liquids, yet it will be the aim of this section to show by calculation based on relatively simple straight-forward assumptions that such forces can exist in polymer blended oils subject to shear.

22. Such a calculation, if correct, will be valuable in that it will indicate where one should begin to expect breakdown, though it will not predict the rate of breakdown.

23. In the calculation, streamline or lamellar flow will be assumed. (A low Reynolds number prevails in most experiments described to date. This confirms the assumption.) Three cases under which breakdown will occur are considered. I. Very dilute solutions, II Dilute solutions, III Conc. solutions.

NOTE: * An interesting experiment to test the action of high local temperatures could be made by observing the extent to which a thermolabile compound of low molecular weight is changed when it is dissolved in the polymer blended oil and subjected to the regular shear breakdown test. A compound which broke down or changed at about 200°C would be desirable. If its transformation paralleled the polymer breakdown, then it would indicate that the effect of high local wall temperatures is important.

24. Case I.* In very dilute solutions, big polymer molecules are far apart and do not come in contact with each other often and so act independently. If a shearing force is exerted on the solution, the parts of the polymer molecule projecting into the various planes of fluid flow will experience forces of varying magnitude. A median plane of flow may be chosen, passing through some central point of our polymer molecule about which the viscous forces balance. (See Fig. III, Plate III) and where the axes may be considered as moving with one point of the molecule. They will have a component of drag on the molecule tending to rotate it about the center and another tending to pull the molecule apart. Axes are chosen that are fixed at some central portion of the molecule and move with it through the liquid medium. Using the simplifying assumptions that: (a) the molecules are rod-like strings of spheres the size of sub-molecules, (b) Stokes Law applies in calculating the viscous drag on the units of polymer chain, (c) the polymer is homogeneous in molecular weight; then the maximum force exerted on the tumbling molecules by the viscous drag may be calculated as:

Equation I

$$F_{\max} = \frac{3\pi}{8} \eta a q L p^2 \text{ dynes (see Appendix)}$$

where η = viscosity of solution (in stokes)

a = radius of submolecule (cm)

q = shear rate of the solution
(sec^{-1})

(Shear rate is velocity gradient per unit distance)

L = distance between centers of sub-molecules (cm)

p = degree of polymer (or no. of sub-molecules in the chain)

For example, in a polystyrene blended oil with

η = 1 stoke ($\frac{\text{dynes sec.}}{\text{cm}^2}$)

a = radius of benzene molecule = 3×10^{-8} cm

q = 10^6 sec^{-1}

L = 2.52×10^{-8} cm

* For a more complete picture see Appendix.

$$P_0 = 1000$$

$$F_{\max} = \frac{1 \text{ dynes sec}^2}{10^{-4} \text{ dynes}} \cdot 3 \times 10^{-8} \text{ cm} \cdot 10^6 \cdot 2.5 \times 10^{-8} \cdot 10^3 \cdot 10^3 = 15 \times 10^3$$

25. This force is seen to be of the same order of magnitude as that required to break a -C-C- bond, namely, 5.5×10^{-4} dynes (as calculated from maximum slope of potential energy curve for -C-C- bond)²⁴. It would then be expected that under such conditions of ' ' and q, breakdown of this polymer due to shear would occur after continued treatment.

26. To apply this equation to more concentrated solutions, it is necessary to introduce terms to account for thermal, and concentration effects, and for the fact that the polymers met with are not homogeneous as regards molecular weight. The resulting equation is

Equation II

$$F_{\max} = K \cdot a \cdot q \cdot L \cdot \frac{\bar{M}_w^2}{M_m^2} \cdot Z$$

where , a, q, and L are defined as before, and

M_m = Molecular weight of monomer

\bar{M}_w = weight average molecular weight of the crude polymer

K = a constant

Z = heterogeneity factor which is unity for homogeneous and about 10 for certain crude polymers.

A more useful form of the equation is:

Equation III

$$Z \cdot \bar{M}_w^2 \cdot q = \frac{F_{\max} M_m^2}{K \cdot a \cdot L} = B$$

where B is called the "breakdown index".

27. If K is evaluated or checked using reliable data, then Equation III becomes a valuable tool if it is desired to set up an apparatus to test for or to avoid viscosity breakdown on a certain polymer blended oil. If the equation is valid, one will be able to predict from theoretical considerations whether or not breakdown will occur. If B, as calculated from $\bar{M}_w^2 \cdot z \cdot \eta \cdot q$, exceeds the theoretical limit for the polymer in question, then appreciable breakdown will be expected.

Case II. Moderately Low Concentrations:

28. In rather more concentrated solutions, the long molecules will become entangled with each other and form small clumps from which attached chain segments stick out. In this case the clump will tend to rotate as a whole making a problem similar to that in dilute solutions. The main difference will be in the position of the point of break. The effect of the projecting lengths makes it more likely that breaks will occur near the ends of the polymer chain, thus yielding unequal fragments. The equation for F_{max} is $\frac{3\pi \cdot \eta \cdot a \cdot q \cdot L \cdot p}{2} \rho^2$ and if $\rho \approx \rho_0$, then

Equation IV

$$F_{max} \approx \frac{3\pi \eta \cdot a \cdot q \cdot L \cdot p_0}{2} \rho_0^2$$

Here, the terms have the same definition as before while p means the number of monomer units projecting from the clump, and where $p_p = p_0$.

29. Breaks near the middle of the chain will occur under the same conditions as before, i.e., where $\rho = \rho_0$. This type of break will produce the greatest change in viscosity per $\frac{1}{2}$ break. Similar equations to Equation III may be set up to describe breakdown.

Case III Concentrated Solutions:

30. Here, the formation of large clumps and networks is considerable. The situation is very complex but the following general statement can be made. The motion, if rapid, will tend to tear apart the interlocking chains before they can disentangle themselves. The breakdown rate will then be a function of the ratio of the shear "q" to the diffusion constant "D" of the segments^{19, 20} of the polymer.

$$\text{rate} = f\left(\frac{q}{D}\right)$$

The shorter the chains, the less the interlocking. The smoother the chains and the less the interaction between chains, the less the rate. In a mixture of unlike chains poor fitting against each other will result, meaning lowered interaction, weaker networks, and less breakdown. This possibly explains why blended polymers are more stable than single polymers in oils.

II. BOUNDARY CONDITIONS FOR SHEAR BREAKDOWN

31. In the calculation of the term B_{lim} useful for the determination of the region where shear breakdown will commence, the terms

F_B = breaking force of weakest bond in chain

M_m = molecular weight of the monomer unit

a = diameter of a sphere having the same viscous drag as monomer unit

L = length between joints of such spheres or length between the ends of the monomer unit that join the chain.

must be evaluated since

$$\text{Eq. III } B_{lim} = \frac{F_B \cdot M_m^2}{(1.2) a \cdot L} = z \cdot M^2 \cdot \eta \cdot q.$$

32. An inspection of the force constants and bond energies of the various bonds met with in commercial polymers shows that with the exception of the -C-S- link, the -C-C- bond is about the same or weaker than any other; therefore, in any polymer containing some C-C links in the main chain, F_B for the -C-C- bond may be used.

Bond	Force Constant (dynes/cm.)	Bond Energy (K cal/mol)	F_B (breaking force in dynes)
C-C (ethane)	5.0×10^5	58.6	5.5×10^{-4}
C-O (ether)	4.5×10^5	70.0	
C-S (thio-ether)	3.0×10^5	54.5	
C-N	4.9×10^5	48.6	
S-S		63.8	
Si-O		89.3	

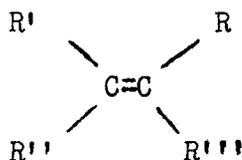
(Force constants taken from Table 19, Theory of Organic Chemistry, Branch and Calvin (1941); Bond energies given on p. 53, Nature of the Chemical Bond, L. Pauling.)

$$\text{For such polymers, } B_{\text{lim}} = \frac{5.5 \times 10^{-4}}{1.20} \cdot \frac{\text{Mm}^2}{\text{a.L}}$$

$$\text{Eq. IV} \quad = 4.6 \times 10^{-4} \cdot \frac{\text{M}^2}{\text{m} \cdot \text{a.L}}$$

33. The evaluation of "a" and "L" must be done individually for each polymer.

For the many polymers resulting from the polymerization of



the value L will be the overall length of the distance between the outer bonds linking the adjoining monomeric groups. For these cases, L = 2.6 Angstroms

34. The evaluation of "a", the diameter of a sphere having the same viscous drag as a monomer unit is difficult. As a rough approximation it is equal to the sum of the radii of the component parts of the molecule considered as spheres. This reasoning is based on the assumption of additivity of viscous drag due to a number of spheres each obeying Stokes Law, i. e.

$$F = 6\pi v \cdot a \cdot \eta$$

$$F = 6\pi v \cdot \eta (a_1 + a_2 + a_3 \dots)$$

where $a = a_1 + a_2 + a_3$; and a_1, a_2, a_3 , etc are the radii

of the several spheres.

35. The following table was constructed to aid in evaluation of "a". To find "a" for a polymer, the structural formula of the monomer was written, the appropriate value of a_i was assigned for each group in the monomers, and summed up. The values of a_i are average diameters of the groups as measured from collision diameters using Fisher-Hirschfelder models.

Group	a_i (in Å)	L (in Å ⁰)
CH	1.0	
CH ₂	1.2	
= C =	0.8	
CH ₃	1.4	
C ₆ H ₅	6.0	
= C = O	1.2	
Si	1.4	
Cl	1.3	
OH	1.1	
-O-	0.9	
H H -C -C-	2.4	2.6
R R Si-O	2.3	3.0

The following table was made using the above means of evaluating F_B , L, and "a".

Polymer	M_m	Structural Formula of Monomer	a	L	B_{lim}
Polyisobutene	56	$\begin{array}{c} \text{CH}_3\text{H} \\ \\ -\text{C}-\text{C}- \\ \\ \text{CH}_3\text{H} \end{array}$	4.6	2.6	1.2×10^{15}
Polystyrene	104	$\begin{array}{c} \text{H} \\ \\ -\text{C}-\text{CH}_2- \\ \\ \text{C}_6\text{H}_5 \end{array}$	8.2	2.6	2.3
Poly methyl acrylate	86	$\begin{array}{c} \text{CH}_2-\text{CH}- \\ \\ \text{C}=\text{O} \\ \\ \text{O} \\ \\ \text{CH}_3 \end{array}$	5.7	2.6	2.3
Polymethyl methacrylate	100	$\begin{array}{c} \text{CH}_3 \\ \\ -\text{CH}_2-\text{C}- \\ \\ \text{C}=\text{O} \\ \\ \text{O} \\ \\ \text{CH}_3 \end{array}$	6.9	2.6	2.6

Polymer	M_m	Structural Formula of Monomer	a	L	B_{lim}
Poly vinyl acetate	86	$\begin{array}{c} \text{H} \\ \\ -\text{CH}_2-\text{C}- \\ \\ \text{O} \\ \\ \text{CO} \\ \\ \text{CH}_3 \end{array}$	5.7	2.6	2.3
Poly vinyl chloride	62.5	$\begin{array}{c} \text{H} \\ \\ -\text{CH}_2-\text{C}- \\ \\ \text{Cl} \end{array}$	3.5	"	2.0
Neoprene	90	$\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ -\text{C}-\text{C}=\text{C}-\text{C}- \\ \quad \quad \quad \\ \text{H} \quad \text{Cl} \quad \text{H} \quad \text{H} \end{array}$	5.5	5.5	1.2
Acryloid (Ethyl methacrylate, methyl acrylate co-polymer)	200	$\begin{array}{c} \text{H} \quad \text{CH}_3 \quad \text{H} \quad \text{H} \\ \quad \quad \quad \\ -\text{C}-\text{C}-\text{C}-\text{C}- \\ \quad \quad \quad \\ \text{H} \quad \text{CO} \quad \text{CO} \\ \quad \\ \text{O} \quad \text{O} \\ \quad \\ \text{CH}_2 \quad \text{CH}_3 \\ \\ \text{CH}_3 \end{array}$	13.8	5.2	2.6
Dimethyl Silicone polymer	74	$\begin{array}{c} \text{CH}_3 \\ \\ -\text{Si}-\text{O}- \\ \\ \text{CH}_3 \end{array}$	5.1	3.0	1.6

36. The terms "a" and "L" may also be evaluated by assuming that the monomeric units are spheres strung along their diameters; then $L = 2a$ and the volume of the monomer unit sphere is $\frac{4}{3}\pi a^3$. This is assumed nearly equal to the volume of the monomeric unit in the pure state of the polymer

$$= \frac{M_m}{d \cdot N_A}$$

M_m = molecular weight of the monomer

d = density of the pure polymer

N_A - Avogadro's number

37. The expression for B_{lim} , the breakdown index value at which polymer breakdown should start, becomes

$$\text{Eq. VI} \quad B_{lim} = z \cdot M^2 \cdot \sqrt[3]{.q} = \frac{F_B \cdot M_m^2}{1.20 \cdot a \cdot L} = F_B \cdot M_m^{4/3} \cdot d^{2/3} \\ \times 7.7 \times 10^{15}$$

$$\text{Eq. VII} \quad B_{lim} = 5.5 \times 10^{-4} \cdot \frac{4}{M_m^3} \cdot d^{\frac{2}{3}} \cdot 7.7 \times 10^{15} = \\ 4.2 \times 10^{12} \cdot d^{\frac{2}{3}} \cdot M_m^{\frac{4}{3}}$$

38. The following table gives B_{lim} for various polymers calculated with this formula. In this case, care must be exercised in the proper choice of M_m , e.g., for copolymers, the average molecular weight of the different monomers must be chosen, otherwise the assumption of sphericity is not met.

Polymer	M_m	$\frac{4}{M_m^3}$	d	$d^{\frac{2}{3}}$	B_{lim}
Polybutene	56	213	1.0	1.0	0.9×10^{15}
Polystyrene	104	493	1.06	1.04	2.2×10^{15}
Poly methyl Acrylate	86	370	1.18	1.12	1.7×10^{15}
" " Methacrylate	100	463	1.18	1.12	2.2×10^{15}
" vinyl acetate	86	370	1.19	1.12	1.7×10^{15}
" " chloride	62.5	246	1.6	1.4	1.5×10^{15}
Neoprene	90	400	1.0	1.0	1.7×10^{15}
Acryloid (Ethyl methacrylate, methyl acrylate copolymer)	100 (av.)	463	1.2	1.13	2.2×10^{15}

39. It may be seen that the values of B_{lim} calculated using either Equation V. or Equation VII are nearly identical. Their agreement serves as an additional check on the basic assumptions. There is a further conclusion to be drawn from inspection of the variation B_{lim} from polymer to polymer. It may be seen that all the values of B_{lim} lie not far from 1.8×10^{15} . This interesting conclusion may be written

Eq. VIII $B_{lim} = z \cdot M^2 \cdot \sqrt[3]{.q} = 2 \times 10^{15}$ for all polymers containing C-C bonds in the main chain. For example, with a polymer of molecular weight 10,000, it would be expected that breakdown should occur when it is subject to a shear of

$$\sqrt[3]{.q} \approx \frac{2 \times 10^{15}}{(10,000)^2} = 2 \times 10^7 \text{ dynes/cm.}^2$$

40. As a corollary of this conclusion it might be pointed out that in searching for a polymer additive that will be superior to others, the variation in chemical structure from one linear polymer to the next will not be a very important factor insofar as the stability to shear forces is concerned. However, the molecular weight, molecular weight distribution, chemical reactivity, and chain branching or cross linking will be relatively far more important for the shear stability of a particular batch of polymer.

III. APPLICATION OF THE THEORY OF BREAKDOWN ONSET

41. It will be interesting to see how closely the equation for breakdown onset fits the facts. It was stated that wherever the breakdown index as calculated from experimental data, using (Equation III) exceeds a certain value, then discernible viscosity breakdown of a polymer blended oil is to be expected under the given experimental conditions and appreciable exposure to them.

42. Available data for testing the equation are scarce and only semi-quantitative. The shear rates and real viscosities in circular tubes are not yet precisely definable where liquids exhibiting anomalous viscosity are undergoing high shear. Molecular weights in the case of the available shear data are only approximate even as to order of magnitude and little is said of the molecular weight distributions. Recent work on polybutenes indicate strongly that the molecular weights given for the polymers examined here are too small by a factor of about four.

43. Despite the nature of the data, calculations based on them might be expected to give at least an order of magnitude check on the validity of the theory.

44. An inspection of tables I and II shows that the breakdown indices as calculated from the experimental data using Equation III fall in the range of 10^{14} - 10^{15} where appreciable breakdown begins. This agrees rather well with the values of about 2×10^{15} calculated theoretically from the molecular constants for the polymers concerned, and invites confidence in the general method of approach. If the molecular weights used were too small by a factor of four then the value of B calculated using the small values is some sixteen fold too small. This brings the experimental and theoretical values very close together.

45. As a further step in examining the data, the percentage breakdown for comparable times of exposure may be plotted against the "breakdown index". If this is done, as in Plate (I), it is

evident that a systematic variation exists, and that wherever "B", the breakdown index, is less than a certain value, very little breakdown occurs. This is further confirmation of the theory.

46. Using Equation III, it is evident why the low temperature Zenith pump tests may produce breakdown even with the relatively low shear rate of 5700 sec^{-1} , for the test is run at such low temperatures (-20 to -80°F) that the viscosity is at the high value of about 10,000 centistokes. Correspondingly, the Pennsylvania Research Laboratory shear viscometer #1 also produces breakdown despite higher temperatures (100°F), for although the viscosity of the same oil is only some 20 centistokes, the shear rates are in the neighborhood of $700,000 \text{ sec}^{-1}$. For a given polymer blended oil containing a crude polystyrene polymer additive of about 35,000 weight average molecular weight, both tests would be expected to produce breakdown. The respective breaking indices would be about 6×10^{15} and 1.4×10^{15} , both about at the theoretical limits of 2×10^{15} . With a polymer of average molecular weight 5000, on the other hand, little breakdown would be expected in either test.

47. It is desired to test the ideas expressed here more thoroughly with further data which, it is hoped, can be obtained in the near future.

To be useful, experimental data should include the following:

- (a) Viscosity at test temperature
- (b) Nature and M.W. of the polymer
- (c) Shear rates to which the polymer blended oil is exposed.
- (d) Test temperature.
- (e) Per cent breakdown of the blend viscosity at 100°F .
- (f) Composition of the blended oil.

Breakdown Rate

48. So far, information has been gained as to when appreciable breakdown would be expected, but little has been said of the rate or extent of it.

If such a theory were available and not too complex for application in the practical use of polymer blended oils, considerable benefit could come from its use. It would presumably be possible to predict and govern the viscosity behavior of any such oil in service,

and to go into research and manufacture with rapidity and with assurance that the final product would meet service requirements.

49. Such knowledge is not yet available, but obtaining it must entail knowing the following:

A. The rate and extent of breakdown of the polymers and the M.W. distribution changes under the given conditions of shear, temperature, and chemical agents.

B. The dependence of the blend viscosity upon the molecular weights of the dissolved polymer and polymer fragments.

50. These facts are not yet known. There are available, however, various empirical rules for the variation of viscosity with molecular weight, the most famous of which is Staudinger's.

$$\eta_{sp} = K_m \cdot M_w \cdot C = \frac{\eta_1}{\eta_0} - 1$$

where η_{sp} = "specific viscosity" of the solution

η_1 = viscosity of the solution

η_0 = viscosity of the solvent

M_w = molecular weight of the linear polymer

C = concentration of submolecules in the solution

K_m = a constant peculiar to each homologous series of polymers. It is reasonably constant above molecular weights of 5000.

51. There is also Eyring's equation for rate processes:

$$\text{rate} = \frac{\text{fraction broken}}{\text{unit time}} = \left(\frac{kT}{h} \right) \cdot \exp - \left(\frac{\Delta F^*}{RT} \right)$$

k = Boltzman constant

T = temperature in degrees absolute

h = Planck's constant

R = gas constant

ΔF^* = free energy of the activated complex - in this case the bond rupturing under shear strain.

52. ΔF^* can be gotten from the theory of breaking tensions developed in this report. It now remains to find the rate of breakdown

for each molecular species, to change that to viscosity terms and sum up the total viscosity changes. This will result in an equation for the change of viscosity with time, shear rate, temperature, chemical agent nature and concentration, initial viscosity, and the initial molecular weight and type of polymer. It can be seen that it will be complex but necessary if a complete solution is to arrived at.

53. With proper regard to experimental conditions it is possible to obtain empirically the above information in a series of experiments. The information gained will almost certainly be of great use in choosing and manufacturing the best obtainable oils.

54. It may be well to digress for a moment to point out an important difference existing between this theory of polymer breakdown caused by shear and the theory of Schmid for breakdown by ultrasonics. In Schmid's theory 14.15, it is necessary that a gel-like network of the chain polymer molecules exist and that the breaking strains be developed by the viscous drag of the small solvent molecules rushing through the mesh under the impact of the sonic waves. Yet if the concentration is low enough or the chain length short enough, no stable network is able to form. This allows the polymer molecules to move with the solvent so that no breakdown occurs. On the other hand, according to the theory presented in this report under shear stresses due to the relative motions of the moving laminae of the fluid medium, no finite concentration minimum or dependence upon gel structure is necessary to have breakdown occur, for enough pull can be exerted even by the pure viscous medium at high shear rates to shear the polymer.

55. The two theories will be parallel in regard to their predicting a lower molecular weight limit which will be reached under continued application of the external forces. Shear breakdown will be facilitated greatly by the formation of a network at higher concentrations where supersonic breakdown is also possible. A difference may be expected between the behavior of very concentrated polymer solutions towards supersonics and shear by other mechanical means. At higher concentrations, solvation holds tightly so great a fraction of the solvent to the polymers that little is left free to move with the waves of sound so that nearly the whole gel structure, solvent and all, moves with the wave front and no great strains are produced to break the polymer chains. This falling off of breakdown with increase of concentration has been observed. Similar observations for the falling off of shear breakdown have not been made in very concentrated

solutions but it is predicted that it will not occur, but that shear breakdown will go on even in very concentrated or pure polymers. As a matter of fact, shear breakdown in pure polymers has been frequently observed. 6, 7, 10.

56. A comment about chemical agents can be made here. In general, the shear forces do not have to equal the breaking strength of the bond to cause rupture, because thermal forces add to them. Furthermore, if there is present a reactive impurity such as O_2 from air which is capable of reacting with the strained but unbroken bond, this would serve as an additional impetus to breakdown.

57. In this connection it may be interesting to note that to react with 100% of the original polymer molecules and produce units having relatively little effect on the blended oil as far as viscosity is concerned, one needs only 0.1 cc of dissolved O_2 per cc of polymer blended oil (M.W. = 10,000, conc. = 4%). This is within the solubility limits of O_2 in oil that is contact with air. (solubility is about 20% by vol.)

58. There are, then, two main factors in shear breakdown that affect the rate. First, mechanical shear forces; second, chemical agents capable of augmenting the mechanical shear forces in breaking a strained molecule. Concerning the first factor, it has already been seen that under given conditions of viscosity and shear rate, the M.W. and type of the polymer are important controls over breakdown of a given polymer. However, it remains possible to minimize the rate of breakdown by controlling the second factor, chemical action. This last can be minimized by a "stabilizer" and the rate of breakdown kept to the minimum amount that is due to mechanical shear forces.

59. It can be seen that though considerable reduction in an observed rate of shear breakdown may be affected by the use of a "stabilizer", there is a well defined limit beyond which such treatment cannot improve the stability of a given polymer blended oil. To go beyond this, there must come improvement in the M.W.'s, types, etc. of polymers blended with the oil.

VI. RECOMMENDATIONS FOR FUTURE ACTION

60. It is suggested that this Laboratory is now in a position to examine and analyze intelligently the problem of the instability

of polymer blended oils under shear, It is recommended:

(1) ~~That~~ experiments be tried here and at other interested laboratories with a view to obtaining data on the rate and extent of viscosity breakdown due to shear, testing in a systematic fashion the various factors important for such shear instability.

(2) That the theory concerning the cause of polymer breakdown suggested herein, be tested further and, if found satisfactory, that service conditions be compared with accelerated laboratory tests to be set up with its aid.

(3) That this Laboratory investigate the possibility of using ultrasonics in testing or producing stable polymer oil additives and patent said process if it proves desirable in order to protect Navy interests.

(4) That these facts and data be gathered and from them Navy specifications be set up for the desired lubricating, hydraulic, and recoil oils.

VII. SUMMARY

61. This Laboratory has attempted to correlate the available facts and to present a reasonable picture of the why and how of polymer breakdown due to shear.

62. The viscosity breakdown of polymer blended oils caused by shear is pictured as involving 3 main factors -- (1) shear forces (2) chemical action (3) thermal forces. The long chain high polymer molecules useful for creating oils of high viscosity and viscosity index are pictured as torn at by the passing layers of the moving medium. The small impact forces are assumed to be added simultaneously along the chain, thus placing important valence bonds under strain. These strains may be aided by thermal motions and perhaps by chemical action to produce bond rupture in the polymer. The resultant short fragments of the polymer have much less ability to create high viscosity and V.I. in their dissolving medium, so both viscosity and V.I. will drop.*

63. A simple rule has been arrived at on theoretical grounds which may serve as an aid to predicting and explaining the presence of appreciable viscosity breakdown. The rule stated simply is: Appreciable viscosity breakdown of a polymer blended oil will not occur if the product (solution viscosity x shear rate x molecular weight

*Only if measured at room temperature or above. At low temperature, due to the drop in V.I., the apparent viscosity of the blended oil may increase with polymer breakdown.

squared), does not exceed a certain limit. This limit apparently can be determined either theoretically or experimentally. It is not expected to apply when chemical agents capable of causing breakdown are active.

64. Various factors affecting the rate and extent of viscosity breakdown have been pointed out. They include, shear rate, viscosity of the blend, molecular weight and type of the polymer, temperature, time, and the composition and concentration of chemical agents present.

65. It was considered possible on theoretical grounds and experimental evidence, to reduce considerably the incidence of unwanted viscosity breakdown of polymer blended oils by:

(1) Addition of stabilizers to cut down chemical action. This will only diminish breakdown for it is basically due to shear strains.

(2) Use of a mechanically stabilized polymer or one of a single well-chosen type and molecular weight.

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APPENDIX

Derivation of Equation for Polymer Breakdown Due to Shear

1. It is the aim of the following calculation to find the maximum force acting on polymer molecules in such a manner as to pull them apart. From this, conclusions can be drawn as to when breakdown of the polymers can be expected to set in. This information should be useful in predicting correlating the behavior of polymer blended oils in actual use.

2. Most authorities on the subject agree that the "straight chain" polymers are much coiled and kinked when in a dissolved state. Such polymers may be thought of as long, thin strings of beads which are usually much tangled due to their random thermal motions. Their average over-all shape will be roughly spherical unless distorted by external forces. If the polymer molecules are in a dilute solution which is undergoing lamellar flow, they will be forced to rotate and at the same time will be squeezed at the middle, while the ends are drawn out by the action of the viscous drag of the medium. Two competing forces determine the exact average shape, the elongating action of fluid flow, and the random thermal motions tending to return the molecule to its original average, spherical shape, See Plate II:

3. As can be seen from the figure, viscous drag of the medium has two components of force; one is radial, tending to pull the molecule apart, and the other is tangential, tending to rotate the molecule. In Newtonian streamline flow, the relative velocity "V" between planes of flow will be proportional to the distance between them, e.g., $V = q \cdot y$, where "q" is a constant, called the shear rate or velocity gradient, and "y" is the distance between planes. For convenience, axes may be chosen as originating in the center of the molecule about which the viscous forces balance. These axes will move with the molecule through the medium.

4. If the molecule is considered as a string of beads or spheres immersed in a homogenous medium, Stokes formula may be used in calculating the viscous drag of the medium on each sphere.

The force exerted on any sphere "i" will be (See Plate IV)

$$F_i = 6\pi \eta A \cdot V_i$$

η = viscosity in stokes

F_i = force in dynes

A = radius in centimeters

V = velocity in centimeters per second

Equation A: $F_i = 6\pi \eta A \cdot Q \cdot V_i$ in a rigid molecule. In a flexible molecule, V_i is not easily determined; however, it will be greater in quadrants I and III than in II and IV because of the rotation of the units about the center in a motion something like that of an endless belt. Since the drag is proportional to the flow rate, the spheres furthest out from the center will experience the greatest drag. The configuration that will experience the greatest force will be that in which the string is stretched out straight and rotating in the x y plane, i.e. when perpendicular to the planes of flow. In order to calculate the maximum force tending to break such a molecule, it is necessary to find the inclination at which this is a maximum on the stretched out molecule.

From Plate III, Equation A, it may be seen that:

$$F_i = 6\pi \eta a \cdot q \cdot r_i \sin \theta_i \text{ and}$$

Equation B:

$$F_i \cdot \cos \theta_i = F_{i,r} = 6\pi \eta a \cdot q \cdot r_i \cdot \sin \theta_i \cos \theta_i$$

5. It may be shown that $\cos \theta \cdot \sin \theta$ has a maximum value of $1/2$ at $\theta = 45^\circ$. This means that the spheres in a rigid molecule of any shape will have exerted on them a maximum radial force at 45° of:

$$F_{i,r,\max} = 3\pi \eta a \cdot q \cdot r_i$$

6. The maximum total force tending to pull any such rigid polymer molecule apart will be:

$$\text{Equation C: } F_{\max} = \sum_{i=0}^{i=\frac{p_0}{2}} \frac{p_0}{2} \quad F_{i,r,\max} = 3\pi \eta a \cdot \sum r_i$$

$$= \frac{3}{2} \pi \cdot p_0 \cdot \eta \cdot a \cdot q \cdot \sum \frac{r_i}{\frac{p_0}{2}}$$

$$\text{Equation D: } = \frac{3}{2} \pi \cdot p_0 \cdot \eta \cdot a \cdot q \cdot x \text{ (average radius)}$$

where p_0 = no. of spheres in chain

7. It can be seen from Equation D that the smaller the average radius, the less the force tending to break the molecule. As a corollary to this, the observation may be made that more compactly built molecules, of otherwise identical nature, would be more stable than linear polymer molecules, which are more easily drawn into long thin shapes by the fluid flow. In this connection, it may be interesting to test branched chain or slightly cross-linked molecules for increased stability to shear. Not only will the force exerted due to fluid flow be less than with linear polymers, but more bonds must be broken to completely shear the molecule. On the other hand, such compact molecules will quite probably exert less influence as viscosity modifiers than linear polymer molecules in the same weight concentration. This would mean that more polymer would be required to do the same job.

8. The extended form will approximate a long, rigid, rod-like molecule. Here, the distance of sphere "i" from the center of rotation will be:

Equation E: $r_i = m_i L$ where "L" is the distance between spheres and " m_i " is the number of units away from the center that sphere "i" stays. The average radius will be $\frac{p_0 \cdot L}{4}$ since m_i goes between the

limits zero and p_0 . Equation D for such a molecular model becomes

$$\text{Equation F: } F_{\max} = \frac{3 \pi}{8} \cdot p_0^2 \cdot \eta \cdot a \cdot L \cdot q; \text{ or, since } p_0 = \frac{M}{M_m}$$

$$F_{\max} = \frac{3 \pi}{8} \cdot \frac{M^2}{M_m^2} \cdot \eta \cdot a \cdot L \cdot q$$

where M = molecular weight of the polymer

M_m = molecular weight of the monomer unit

9. This will be the maximum force tending to break a rod-like molecule and will be the maximum possible tension exertable on a flexible molecule, provided the basic assumptions are correct.

10. The random thermal motions of the molecules and the action of chemical agents on the bond activated by mechanical strain both induce more rapid breakdown than would occur under mechanical strain alone. At room temperature, the first will be a small order effect, but above about 100°C will become appreciable. Since most tests are run near room temperature or lower, however, this factor may be ignored for convenience of approximation.

11. The effect of chemical agents may be powerful and is likely to be greatly variable. It cannot be taken into account here. If break-

down occurs under otherwise mild mechanical conditions, chemical action may be suspected.

12. The equation (Equation F) for the maximum force tending to break the central bonds was derived on the assumption that the solution was so dilute that contact between the polymer molecules was rare. If it is applied to cases where the concentration is so high that the long chain polymer molecules become entangled in each other, it is expected that the rate and extent of breakdown will be increased by the concentration and that less severe mechanical shear by the solution will serve to break the polymer than if no entanglement occurs. The effect will be of varying magnitude from one concentration to the next. Evaluation of it will be difficult.

13. The breaking force calculated by Equation F is specific for the molecular weight (M) of the polymer species assumed. In a mixture of polymers such as in a batch of crude polymer, however, many species of widely varied M exist. Application of the equation can be made only if the distribution and magnitude of the M 's are known. A hypothetical M can be used to account for the preferential breakdown of high molecular weight fractions, and for the correspondingly greater sensitivity of the loss in solution viscosity when the bigger molecules break. The molecular weight distribution may vary with the method of preparation. That value of " M " obtained from viscosity measurement is approximately the weight average molecular weight, \bar{M}_w . (50% by weight is lower, and 50% is higher than the average.)

14. If, for example, the crude polymer samples examined have M_z distributions like those of the crude samples examined by G. V. Schulz,^{21,22} then some 10% by weight is more than double and about 1% is more than triple the weight average molecular weight, \bar{M}_w .

15. The choice of a hypothetical M for such a crude polymer will be that M which produces the first appreciable viscosity loss on shear. In such batches this will be roughly $3\bar{M}_w$ and $\frac{1}{2}$ since M enters as the square into the equation for the breaking force, $10\bar{M}_w$ may be introduced to replace M^2 and to account roughly for molecular weight heterogeneity.

16. To sum up, the various factors for 3π for thermal motion, and for entanglement of chains, may be replaced δ by a constant, " K ". The effect of chemical action is left unaccounted for. That factor due to varying molecular weight distributions, is introduced by a term, " z ", which will be unity for homogeneous samples of polymer, and about 10 for crude. The resulting equation is:

$$\text{Equation G: } F_{\max} = \frac{k.n.a.L.q.z}{M_m^2} \cdot \bar{M}_w^2$$

17. This equation may be put in a more useful form:

$$\text{Equation H: } \eta q z \bar{M}_w^2 = \frac{F_{\max} \cdot M_m^2}{\text{k.a.l.}} = B$$

Where "B" is defined as the "breakdown index."

TABLE I

Source of Data	Polymer*	\bar{M}_w	Visc. at test temperature (Stokes)	Shear rate (sec ⁻¹)	Calculated Breaking Tension $\frac{\bar{M}_w}{z}$ n.q.z. (z=10)	Visc. Breakdown (%)	Type of app. Used in Test	Remarks
Ref. #3 p. 55	PB	1260	(0.4)	723,000	4.6 x 10 ¹⁴	6	Shear viscom. #1	See Fenske's Report #3 Nov. 1941 (2 Sec. shear)
p. 55	"	5,320	(0.5)	"	1.0 x 10 ¹⁴	0.4		
p. 111	"	12,600	0.11	"	1.3 x 10 ¹⁴	0.0		
"	"	"	0.22	"	2.5 x 10 ¹⁴	0.0	"	
"	"	"	0.21	"	2.4 x 10 ¹⁴	0.6	"	
"	"	5,320	0.23	"	4.7 x 10 ¹³	0.0	"	
Ref. #5 f (loose sheets) P. 3	"	14,900	100	11,200	2.5 x 10 ¹⁵	40	Zenith Gear pump & Capillaries	
"	"	12,200	100	11,200	1.7 x 10 ¹⁵	30	"	
Ref. 23 P. 5	"	(12,600)	0.14	740,000	1.7 x 10 ¹⁴	1.5	Shear Visc. #1	2 sec. shear
"	"	"	0.12	"	1.4 x 10 ¹⁴	0.0	"	"
"	"	"	0.18	692,000	2.0 x 10 ¹⁴	2.4	"	"
"	"	"	0.16	726,000	1.9 x 10 ¹⁴	0.7	"	"
"	"	5,000	0.17	730,000	3 x 10 ¹⁴	0.7	"	"
"	"	12,600	0.13	740,000	1.6 x 10 ¹⁴	0.7	"	"

*PB = Polybutene

TABLE II

Source of Data	Polymer*	\bar{M}_w	Visc. at test temperature. (Stokes)	Shear rate (sec. ⁻¹)	Calculated Breaking Tension $\frac{\bar{M}_w}{z}$ n.g.z. ($z=10$)	Visc. Break-down (%)	Type of App. Used in Test	Remarks
Ref. #5g, Table I	PS	12,000	14.0(?)	5700	1.2×10^{14}	6.8	Zenith gear pump and capillaries	300 passes in pump (controller oil) PS (controller oil PS) 325 min.
" #5D, Table I	"	12,600	64	"	5.8×10^{14}	6.8	"	
" #5e, Table IV	"	15,000	14	"	1.8×10^{14}	6.8	"	
" #5a, Page 5	"	36,000	(23)	"	1.7×10^{15}	46	"	
"	"	17,200		"				
"	"	(homogenized)	(20)	"	3.4×10^{13}	0	"	
"	"	14,800	(37)	"	4.6×10^{14}	13	"	
" #5c, "	"	55,000	(14)	"	2.4×10^{15}	50	"	Sample after shear test above. 325 min.
"	"	16,600	(14)	"	2.2×10^{13}	0	"	Refer to the data of 5th line of data. 325 min.
" #5b, "	"	15,200	(17)	"	2.2×10^{14}	17	"	

*PS = Polystyrene

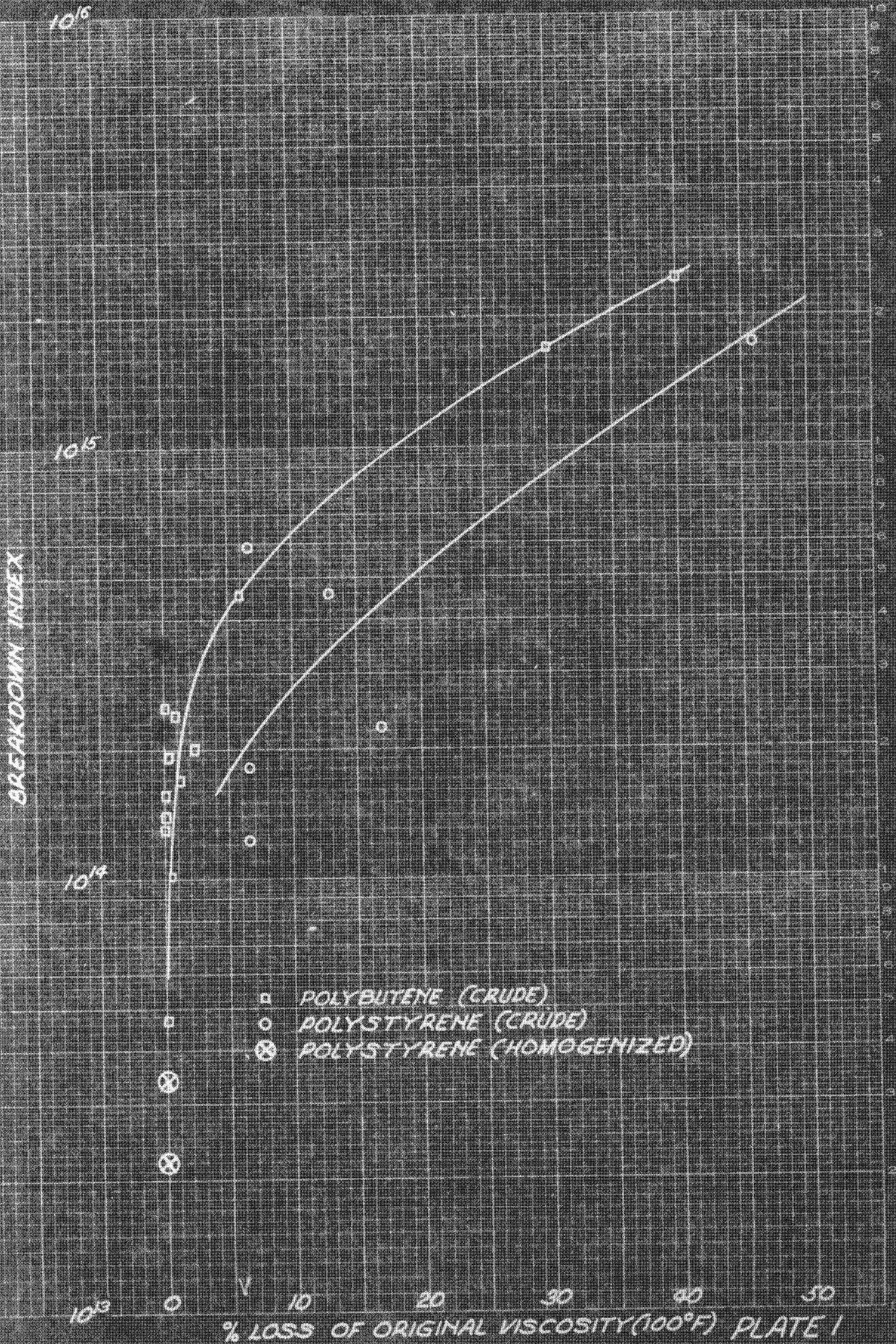
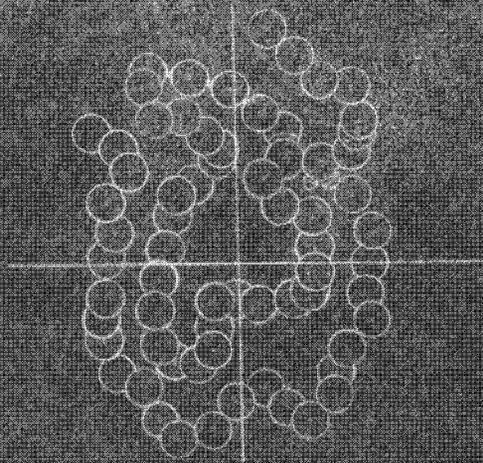


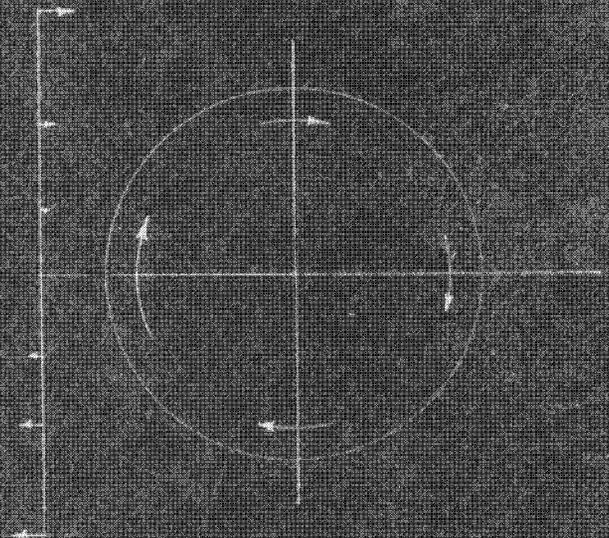
FIG. 1



A POLYSTYRENE MOLECULE
(M.W. \approx 7000)

POLYMER MOLECULES
IN SOLUTION

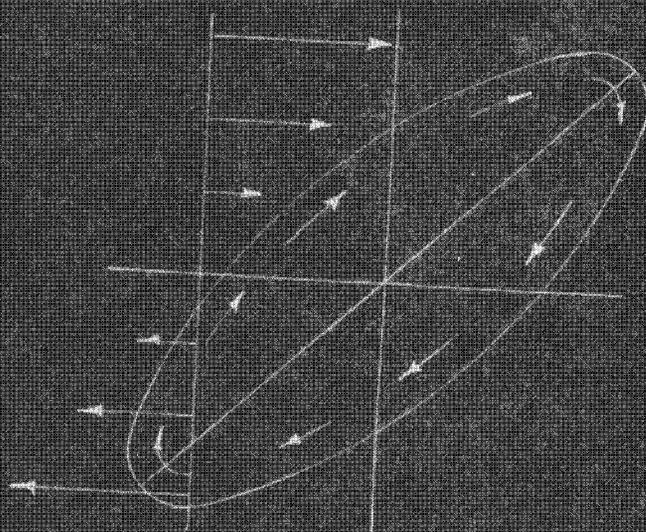
FIG. 2



(ARROWS INDICATE
DIRECTION AND
MAGNITUDE OF FLOW
IN MEDIUM AND IN
MOLECULE.)

AVERAGE SHAPE AT
REST OR UNDER VERY
LOW SHEAR.

FIG. 3

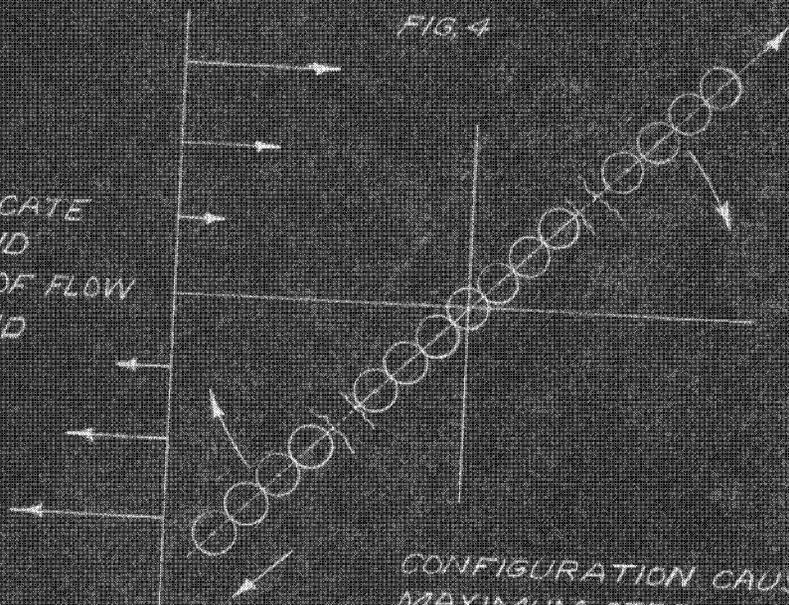


POLYMER MOLECULES
IN SOLUTION

AVERAGE SHAPE
UNDER HIGH SHEAR

FIG. 4

(ARROWS INDICATE
DIRECTION AND
MAGNITUDE OF FLOW
IN MEDIUM AND
IN MOLECULE)



CONFIGURATION CAUSING
MAXIMUM STRESS AT
CENTRAL BONDS.

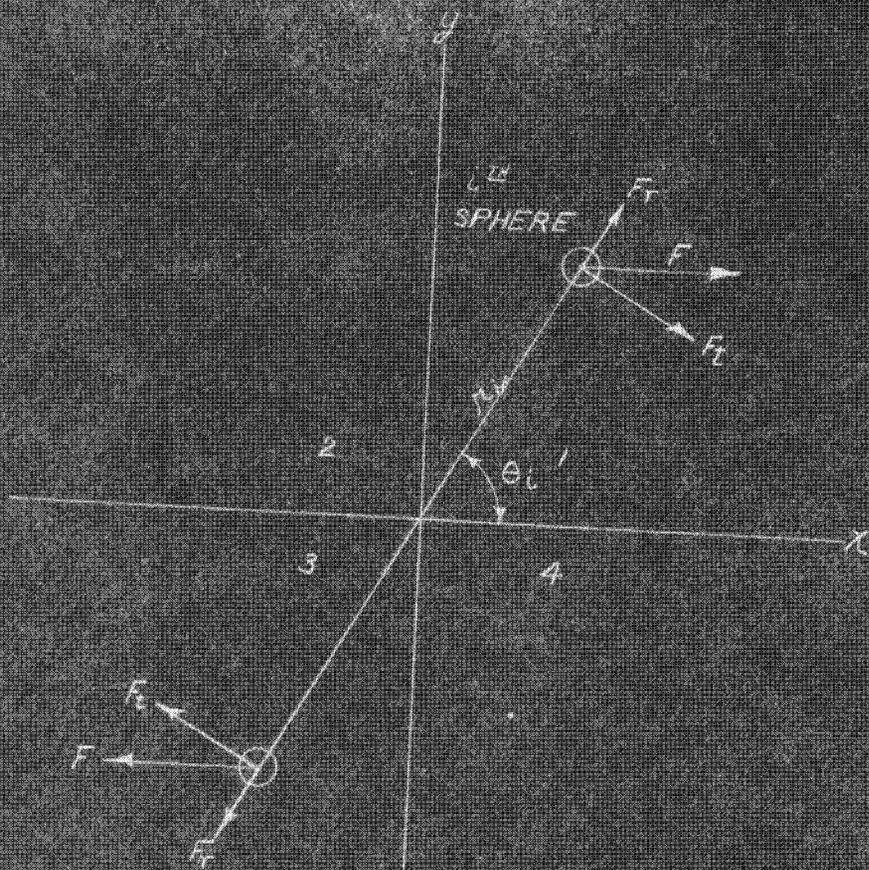


DIAGRAM OF THE FORCES EXERTED BY THE FLOWING MEDIUM ON EACH UNIT OF A POLYMER MOLECULE.

- F : VISCOUS DRAG
- F_r : RADIAL COMPONENT CAUSING ROTATION
- F_t : TANGENTIAL COMPONENT TENDING TO PULL MOLECULE APART.