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The Retardation of Drop Breakup in High-Velocity Airstreams by Polymeric Modifiers

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The breakup of liquids in high-velocity airstreams is being studied under conditions similar to those that occur in spray from high-speed aircraft and in explosive dissemination. This report is the second of a series on drop breakup studies. In the first report of this series[1] the apparatus built for these studies was described. This apparatus, consists of a miniature vertical shock tube. By use of this apparatus, drops of liquid were subjected, very conveniently, to controlled high-velocity airstreams.

A number of investigators, including Lane,[2] Priem,[3] Hanson and Domich,[4] and, most recently, Engel[5] have studied the breakup of liquid drops when subjected to high-velocity airstreams. All of these investigators have worked with Newtonian liquids. In the work described in this report, the breakup of non-Newtonian (viscoelastic) liquids was investigated.

A liquid drop in an airstream is acted upon, for purposes of simplicity, by two forces. These forces are the internal forces tending to hold the drop together, and the external forces tending to tear the drop apart. Factors such as surface tension, viscosity, elasticity, initial size of the mass, and aerodynamic forces influence the stability of a free falling drop. However, when the relative velocity between the airstream and the drop is high enough to overcome the internal forces, the drop becomes unstable and breaks up. The mechanism of breakup depends upon how greatly the velocity exceeds the minimum velocity required to produce instability.

High-velocity airstreams cause the breakup of Newtonian liquids into extremely small particles. This type of breakup is shown in the previous report,[1] by other investigators,[2–5] and in Figure 1. These small particles have a low settling velocity and therefore remain air-borne for relatively long periods of time. There are several applications involving the spray of liquids where such small particles are not desirable.

In the case of an aircraft spraying insecticide it is desirable to place the insecticide on the ground in a relatively short period of time. If a great number of fine particles are produced, the prevailing wind may carry them away from the area.

In the case of the formation of a smoke screen by spraying chemical smoke screen agents from high-velocity aircraft it is desirable that some particles of liquid be large enough to reach the ground before the reaction in air is complete so as to produce a complete smoke curtain.

Certain studies in the field of combustion indicate that it is also desirable to eliminate the fine particles from sprays of fuel to obtain controlled burning and optimum efficiency.[6–9]

There are several possible methods by which the retarding of the breakup of liquids by high-velocity airstreams may be accomplished. These methods involve either use of specially designed spray equipment or alteration of the physical properties of the liquid by addition of soluble polymers. In this work the effect of soluble polymeric modifiers in retarding the breakup by high-velocity airstreams was studied.

EXPERIMENTAL

The liquids selected for this study were bis(2-ethyl hexyl) hydrogen phosphite and dibutyl phthalate and will be referred to as BIS and DBP, respectively. Solutions in these liquids of the following polymeric modifiers were used in this study: (a) polyisobutyl methacrylate (AE polymer, a high molecular weight polymer made by DuPont Co. during World War II); (b) polyvinyl acetates (Lemac 1000 and Lemac 100 grades made by

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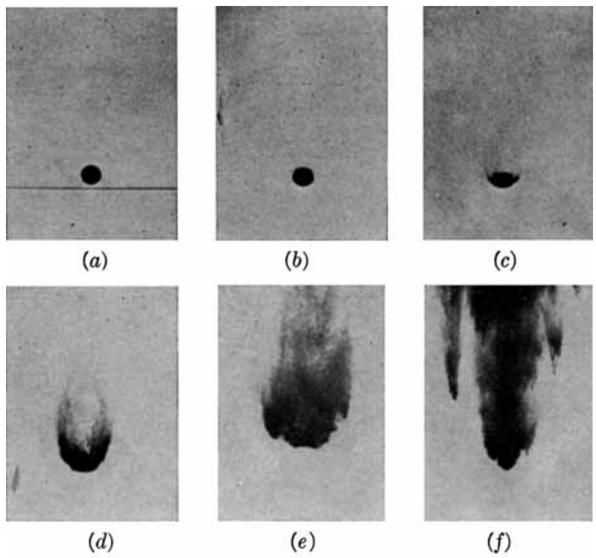


Fig. 1. Breakup of a 3-mm. drop of BIS, airstream velocity 1200 ft./sec.: (*a*) 0 μsec.; (*b*) 70 μsec.; (*c*) 150 μsec.; (*d*) 250 μsec.; (*e*) 490 μsec.; (*f*) 850 μsec.

Borden Chemical Co.); (c) nitrocellulose (a highly nitrated, high molecular weight grade, Hercules 377).

Shock Tube and Experimental Apparatus

A block diagram of the shock tube and timing equipment is shown in Figure 2. The experimental procedure and some theory of operation of this shock tube is given in detail in the previous report.[1] A brief description is given below.

A drop is formed from a modified hypodermic needle mounted inside the vertical shock tube. Upon release of the drop it falls down the evacuated expansion chamber. In its fall it breaks the path of a light beam to a photocell and the resulting impulse is delayed and amplified. This delayed impulse is used to activate a solenoid upon which a sharp dagger is attached. The dagger breaks the frangible diaphragm separating the compression and expansion chambers. The pressures of these chambers have been previously adjusted to give the desired airstream velocity and pressure during the test. Rupture of the diaphragm causes the formation of a shock front which progresses rapidly up the expansion chamber. Following the shock front is a zone of uniform, high-velocity airflow, which is used for our test purposes. As the shock front progresses up the expansion chamber, its passage is sensed by a crystal pickup. This impulse is also delayed and amplified and used to trigger the spark unit. The firing of the high voltage spark unit results in exposure of a piece of photographic film to produce a shadowgraph of the drop. With the proper delay times set into the equipment one can cause the desired event to occur at the photographic observation window.

The size of the drops used in these tests was 3 mm. in diameter. The airstream was usually traveling at 1200 ft./sec., with the exception of the few tests which were conducted at 721 ft./sec. (0.5 Mach).

Breakup of Newtonian Liquid

Figure 1 shows the action of a high velocity airstream on a drop of a Newtonian liquid, BIS in this case. The times given in the figure are in microseconds after passage of the shock front. The breakup mechanism observed is the same as that observed and described by Lane[2] and Engel[5] in their studies with water drops. In the time up to about 150 μsec. after passage of the shock front, the leading surface remains convex upstream as the downstream side flattens to a planer shape and stripping of small droplets from the surface begins. Then the small droplet cloud grows, the deformations increase, and a chaotic disintegration of the remaining particle bulk occurs until the fragments are accelerated to the velocity of the air flow. The initial mechanism of breakup involves predominantly surface stripping of the drop.

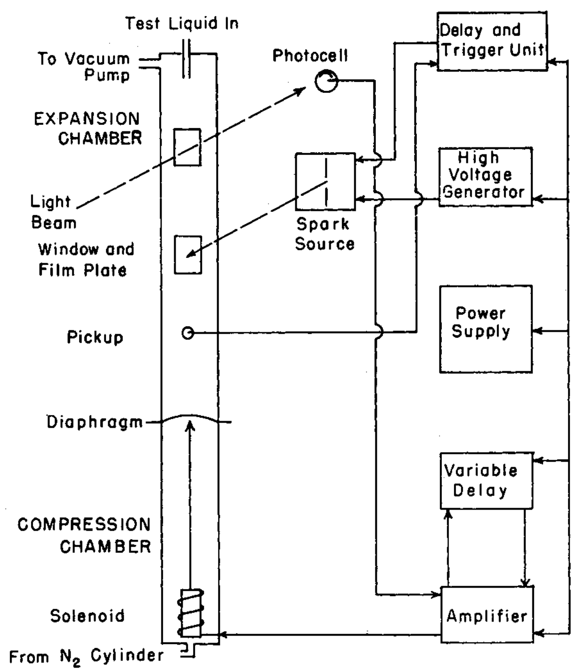


Fig. 2. Block diagram of shock tube.

Breakup of Non-Newtonian (Viscoelastic) Liquids (Polymer Solutions)

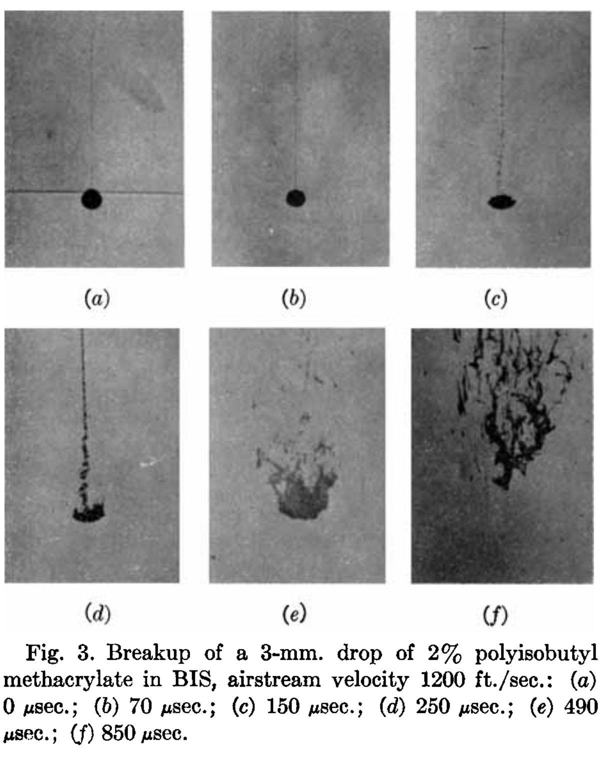
As mentioned earlier in this report, the main purpose of this work was to study the use of soluble polymers to retard the breakup of liquids by high velocity air streams. In the work to date, three polymeric-modifiers were found to be useful in delaying the breakup of liquids in high-velocity airstreams. The results obtained with these polymers are given in the following paragraphs.

RESULTS

Effect with Polyisobutyl Methacrylate Solutions

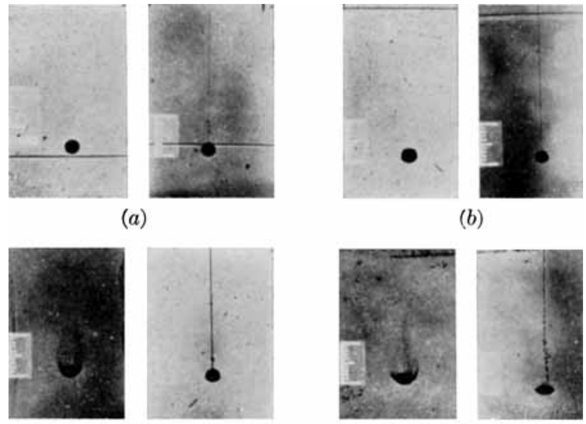
Figure 3 shows the action of a high-velocity airstream on a drop of a viscoelastic liquid, a 2% solution of polyisobutyl methacrylate in BIS.

Photographs of the breakup behavior of a 2% solution of polyisobutyl methacrylate in BIS were compared with those of BIS alone. Figures 4 and 5 show this comparison, the photographs labeled U showing the breakup of BIS alone, and those labeled T show the breakup of the polymer solution. The times given in these figures are in microseconds after passage of the shock front or the exposure time of the liquid drop to the forces of the high velocity airstream.



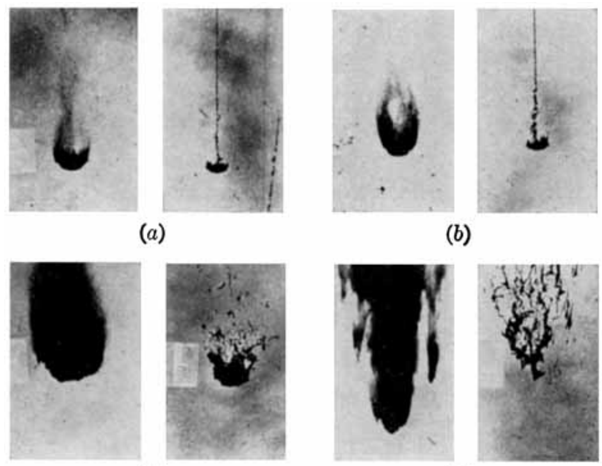
(a) (b) (c) (d) (e) (f)

Fig. 3. Breakup of a 3-mm. drop of 2% polyisobutyl methacrylate in BIS, airstream velocity 1200 ft./sec.: (a) 0 μsec.; (b) 70 μsec.; (c) 150 μsec.; (d) 250 μsec.; (e) 490 μsec.; (f) 850 μsec.



(a) (b) (c) (d)

Fig. 4. Breakup of drops of BIS alone (left photo of each pair) and 2% polyisobutyl methacrylate in BIS (right photo of each pair), time intervals 0–130 μsec.: (a) 0 μsec.; (b) 60 μsec.; (c) 80 μsec.; (d) 130 μsec.



(a) (b) (c) (d)

Fig. 5. Breakup of drops of BIS alone (left photo of each pair) and 2% polyisobutyl methacrylate in BIS (right photo of each pair), time intervals 170–760 μsec.: (a) 170 μsec.; (b) 220 μsec.; (c) 430 μsec.; (d) 760 μsec.

The shadowgraphs in Figures 4 and 5 show quite clearly that the polyisobutyl methacrylate additive retards breakup of the liquid drop in every stage. In the final stages, the breakup occurs by formation of ligaments rather than by surface stripping, as was the case with the BIS alone.

In the case of the pure BIS, also shown in Figures 4 and 5, disintegration occurs resulting in extremely small particles. In the case of the BIS–polymer solution, breakup by ligament formation occurs, resulting in formation of rather large particles with few, if any, small particles. The particle size was qualitatively determined. The pure BIS resulted in particles of 10 μ diameter and smaller, while the BIS–polymer solution gave particles 1.5 orders of magnitude larger (estimated average of 500 μ).

Effect of Polymer Concentration

Figure 6 shows a series of shadowgraphs in which the polymer concentration was varied from 0 to 2%. It is interesting to note that quantities of polymer as low as 0.1% show some effect in inhibiting the breakup.

For this comparison, photographs were used which were taken at a time interval of 500 μsec. after the passage of the shock front. This time interval was used for all comparisons of this type, since it was found to permit a representative evaluation of the effect of a particular polymer concentration or molecular species.

Effect of Airstream Velocity

Figure 6 shows the breakup of a liquid drop under the action of an airstream traveling at a velocity of 1200 ft./sec. (approximately Mach 1). In Figure 7, the velocity of the airstream is reduced to 721 ft./sec. (approximately 0.5 Mach). At both velocities retardation of drop breakup and breakup by ligament formation is shown. As would be expected, the retarding effect is more pronounced at the lower velocity since the relative velocity between the airstream and the drop was lower.

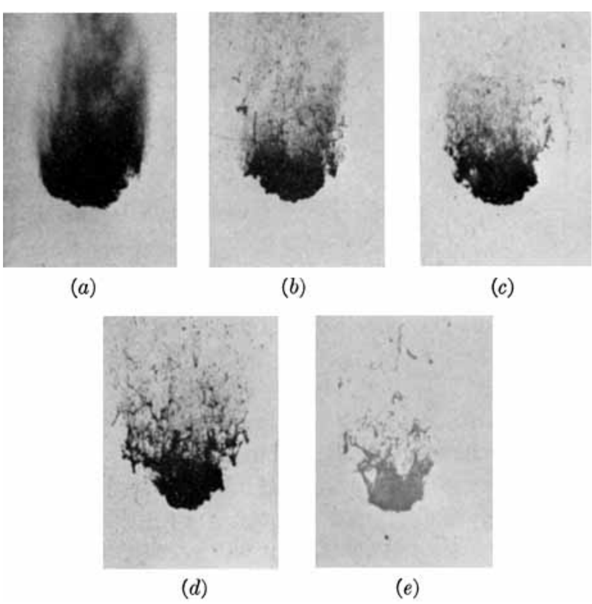


Fig. 6. Effect of polymer concentration on breakup of 3-mm. drops of polyisobutyl methacrylate in BIS, airstream velocity 1200 ft./sec., time interval 500 μsec.: (*a*) 0%; (*b*) 0.1%; (*c*) 0.5%; (*d*) 1.0%; (*e*) 2.0% polymer.

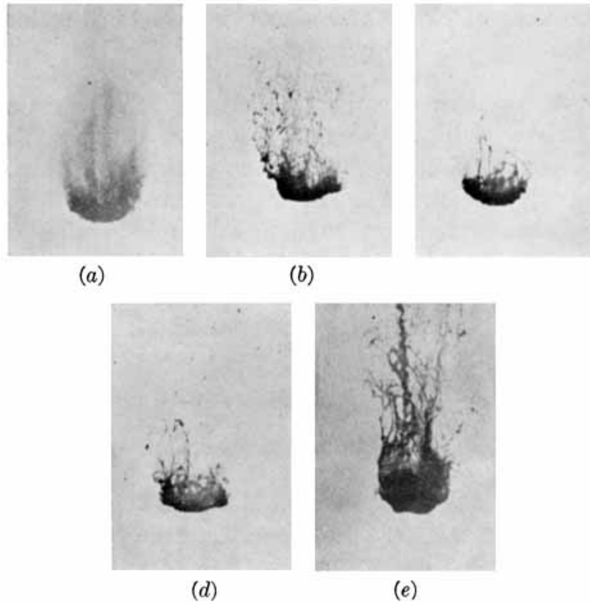


Fig. 7. Effect of polymer concentration on breakup of 3-mm. drops of polyisobutyl methacrylate in BIS, airstream, velocity 721 ft./sec., time interval 500 μsec.; (*a*) 0%; (*b*) 0.1%; (*c*) 0.5%; (*d*) 1.0%; (*e*) 2.0% polymer.

Effect with Polyvinyl Acetate Solutions

Figure 8 shows the action of a high-velocity airstream on two types of polyvinyl acetate (Lemac 100 and Lemac 1000) in solution in dibutyl phthalate (DPB) at concentrations from 0.02 to 2.0%. On examination of these shadowgraphs it is noted that these particular polyvinyl acetates impart a marked breakup inhibition effect. As with polyisobutyl methacrylate, the effectiveness decreases as the concentration of the polymer is lowered. Even at a concentration of 0.1% the effectiveness is quite evident. At 0.02% concentration there is only a slight effect. One would predict from the previous experiments that the retarding effect at 0.02% would be more pronounced at lower airstream velocities.

Effect with Nitrocellulose Solutions

Figure 9 shows the marked breakup inhibiting effect of nitrocellulose (Hercules 377) at concentrations from 0.02 to 0.5%. However, this material is not considered a potentially satisfactory breakup inhibitor because of its instability and inflammability.

Effect of Viscosity on Drop Breakup

In order to get a picture of the effect of viscosity change on drop breakup, paraffin oil was added to

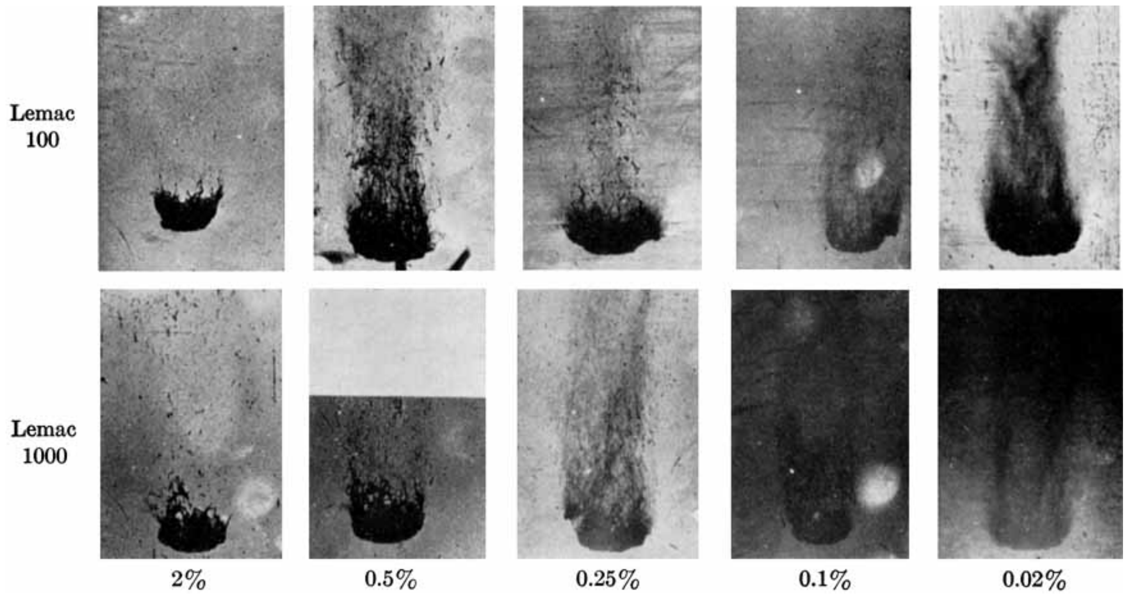


Fig. 8. Effect of polymer concentration on breakup of 3-mm. drops of polyvinyl acetates in DBP, airstream velocity 1200 ft./sec., time interval 500 μsec.

BIS, with a resulting increase in viscosity. Figure 10 is a series of shadowgraphs showing BIS alone, a paraffin oil in BIS, and paraffin oil alone in a drop breakup experiment. There was no significant breakup difference although the viscosity was increased by a factor of approximately 25.

DISCUSSION

This study of drop breakup in high velocity airstreams has shown that it is possible to retard drop breakup by the addition of small quantities of polymers which impart viscoelasticity. All of the polymers used in the work described in this report were found to be effective in retarding drop breakup. These polymers were shown to be effective in concentrations as low as 0.1%.

The search for suitable polymers has been limited to polymers soluble in selected liquids and having a high molecular weight. One might predict that polymers that showed no inhibition effects, when exposed to airstreams having a velocity of Mach 1, might show desirable effects at lower airstream velocities and/or at concentrations higher than 2%.

These drop breakup experiments indicate that the use of polymers which impart viscoelastic properties in dilute solution appears to be a feasible method for retarding liquid breakup in spraying of liquids under high velocity conditions. The method would involve only a very small reduction in "payload" and would be applicable for use with liquid insecticides and other liquids. It might also be possible to control, within limits, the size dis-

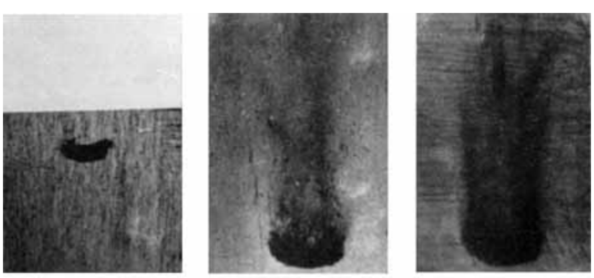


Fig. 9. Effects of polymer concentration on breakup of 3-mm. drops of nitrocellulose (Hercules 377) in DBP, airstream velocity 1200 ft./sec., time interval 500 μsec.: (*a*) 0.5%; (*b*) 0.1%; (*c*) 0.02% polymer.

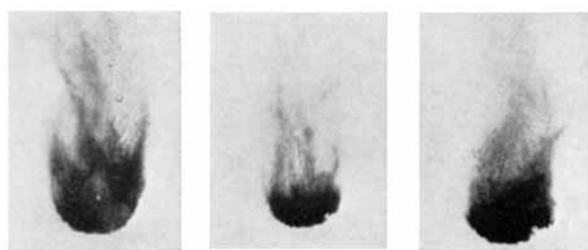


Fig. 10. Effect of viscosity on breakup of 3-mm. drops of BIS, a BIS–paraffin oil mixture, and paraffin oil alone, airstream velocity of 1200 ft/sec., time interval 500 μsec.: (*a*) 100% BIS, 6.25 cpoise; (*b*) 25.42% oil in BIS, 10.34 cpoise; (*c*) 100% oil, 159.7 cpoise.

tribution of liquids broken up by high-velocity atomization.

CONCLUSIONS

Polymeric modifiers that produce viscoelastic properties (non-Newtonian) in solutions retard the breakup of the liquid when subjected to high-velocity airstreams (up to at least Mach 1).

Certain types of polyisobutyl methacrylate, polyvinyl acetate and nitrocellulose in concentrations as low as 0.1% of polymer are effective in inhibiting the breakup of liquids by high velocity airstreams.

References

1. Wilcox, J. D., and R. K. June, "Apparatus for study of the breakup of liquid drops by high velocity airstreams," unpublished.

2. Lane, W. R., *Ind. Eng. Chem.*, **43,** 1312 (1951).

3. Priem, J., *Jet Propulsion*, **27,** 1084, October 1957.

4. Hanson, A. R., and E. G. Domich, Research Report No. 125; Research Report No. 130, University of Minnesota, Rosemount Aeronautical Laboratories, 1956.

5. Engel, G., *Research Natl. Bur. Standards,* **60,** 245 (1958).

6. Spalding, D. B., *Some Fundamentals of Combustion,* Academic Press, New York, 1955, p. 142.

7. Thring, M. W., and M. P. Newby, *Fourth Symposium (International) on Combustion, Cambridge, Mass.*, 1952, Williams & Wilkens, Baltimore, 1953, p. 789.

8. Anson, D., *Fuel,* **32,** 39 (1953).

9. Burgoyne, J. H., and L. Cohen, *Proc. Roy. Soc. (London),* **A225,** No. 1162, 375 (1954).

Synopsis

Investigations are being conducted on the factors involved in the breakup of Newtonian and non-Newtonian (viscoelastic) liquids in high velocity airstreams. Viscoelastic solutions are formed by the addition of small amounts of polymeric modifiers to the test liquid. The mechanism of breakup is shown to be significantly different between the thickened and unthickened solutions. It was found that Newtonian liquid drops are broken into very fine particles by a breakup mechanism which begins with a stripping of the liquid from the surface of the drop. On the other hand, drops of non-Newtonian liquids break up by formation of ligaments rather than by surface stripping and are broken into much larger particles. An increase in viscosity by a factor of 25 in the Newtonian liquids showed no significant change in the breakup mechanism.

Résumé

On a effectué des recherches sur les facteurs impliqués dans l'éclatement des liquides Newtoniens et non Newtoniens viscoélastiques dans des courant d'air de grande rapidité. On a formé des solutions viscoélastiques par l'addition de petites quantités de modificateurs polymériques au liquide à examiner. Le mécanisme d'éclatement est notablement différent suivant qu'il sagit d'une solution épaissie ou non épaissie. On a trouvé que les gouttes de liquide Newtonien sont brisées en très petites particules par un mécanisme d'éclatement qui commence par le départ du liquide de la surface de la goutte. Par ailleurs, les gouttes des liquides non-Newtoniens éclatent par formation de ligaments plutôt que par dépouillement de la surface et elles sont brisées en particules de plus grande dimension. Quand la viscosité du liquide Newtonien est accrue d'un facteur de 25, il n'y a pas de changement notable dans le mécanisme d'eclatement.

Zusammenfassung

Untersuchungen über die Faktoren, die für die Zerteilung von Newton'schen und nicht-Newton'schen (viskoelastischen) Flüssigkeiten in Luftströmen hoher Geschwindigkeit bestimmend sind, werden durchgeführt. Viskoelastische Flüssigkeiten werden durch Zusatz kleiner Mengen von polymeren Stoffen zur Testflüssigkeit erhalten. Es wird gezeigt, dass der Zerteilungsmechanismus sich bei verdickten und unverdickten Flüssigkeiten in charakteristischer Weise unterscheidet. Wie gefunden wird, ertilen sich Tropfen einer Newton'schen Flüssigkeit durch einen Zerteilungsmechanismus, der mit einem Abstreifen der Flüssigkeit von der Oberfläche des Tropfens beginnt, in sehr feine Partikeln. Andrerseits zerteilen sich Tropfen einer nicht-Newton'schen Flüssigkeit eher durch Bandbildung als durch Abstreifen der Oberfläche und werden in viel grössere Partikel aufgespalten. Eine Viskositätszunahm einer Newton'schen Flüssigkeit auf das 25fache zeigte keine charakteristische Änderung des Zerteilungsmechanismus.

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