A RHEOLOGICAL STUDY OF THE EFFECT OF BENTONITE ON HEATED EMULSIONS

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In a preliminary study on a number of cream bases it was found by the author that the addition of a small amount of bentonite to the formula made it possible for these emulsions to be sterilised by autoclaving without creaming or separation of the oil phase[1,2]. The autoclaved emulsions, with and without bentonite, differed markedly in physical appearance and in consistency. An attempt has been made in this paper to assess the observed difference quantitatively and to present a technique of general application for the determination of the consistency of semi-solid preparations of pharmaceutical interest. The measurement of the consistency of semi-solid preparations has presented difficulties in the asphalt, dairy, paint, pharmaceutical, printing ink, and rubber industries. Organoleptic tests which are dependent on subjective assessment by such methods as stirring with a spatula, or tapping out on to a porcelain slab, were among the first methods to be used to assess consistency, and are still employed to some extent. The evaluation of these tests often depends on acquired skill. Simple instruments which give empirical results, e.g., flow cups, and penetrometers, are also used in many different forms in the various industries. These "single point" methods are used for convenience, primarily because they are quickly performed and require neither elaborate instruments nor acquired skill. The correlation between subjective assessment and empirical methods of testing is often difficult and sometimes misleading[3]. It is not possible with these "single point" methods to distinguish between Newtonian flow which is independent of the rate and time of shear, and anomalous viscosity which is dependent on the rate of shear and in some instances on the time of shear. It is very important that these differences in behaviour should be recognised in the assessment and study of systems showing anomalous viscosity. In this paper the importance of the rate of shear in the determination of the viscosity of emulsions is illustrated. In further work it is intended that some of the factors which are known to affect the consistency of emulsions will be experimentally investigated.

The viscosity of emulsions in laminar flow can be characterised by a rate of shear—shearing stress curve called a viscosity curve. The different types of anomalous behaviour which are found in pharmaceutical preparations such as emulsions and suspensions are illustrated by the viscosity curves A, B, and C, shown in Figure 1.

Curve A. Uniform plastic flow. The viscosity curve shows an intercept T_2 on the shearing stress axis, i.e., a yield stress or yield value below which no laminar flow occurs. The observed viscosity above this stress is constant; the rate of flow is proportional to the shearing stress.

Curve B.   Shear-rate thinning.   The viscosity curve passes through the origin indicating that flow occurs at an infinitely low stress.   The observed viscosity decreases with increased rate of shear and approaches a constant value asymptotically.

Curve C.   Shear-rate thickening.   The viscosity curve passes through the origin indicating that flow occurs at an infinitely low stress.   The observed viscosity increases with increased rate of shear.

Some systems which show anomalous viscous behaviour, as described above, are also dependent on the time of shear. This dependence on the time of shear is described as thixotropy and the curves A, B, and C, will then be typical of a family of curves.   These several types of anomalous viscous behaviour have been described in numerous rheological studies on suspensions of insoluble powders by Green[4,5], Weltmann[6,7], and Mardles[8].

FIG. 1.   Viscosity curves typical of preparations showing anomalous behaviour.
A.   Uniform plastic flow.
B.   Shear-rate thinning.
C.   Shear-rate thickening.

Hatschek[9] was the first to stress the importance of the rate of shear at which the viscosity of an emulsion was determined.   He showed that the viscosity of an emulsion varied with the rate of shear.   The observed viscosity decreased as the rate of shear increased and became almost constant at high rates of shear.   This type of anomalous behaviour would be described under the present terminology as shear-rate thinning.   These results have been confirmed by the following workers using different emulsion systems.

Broughton and Squires[10] used emulsions of (1) liquid paraffin, (2) benzene, and (3) olive oil, emulsified with each of the oil-in-water emulsifying agents saponin, sodium oleate, and triethanolamine oleate. Krieger and Maron[11] used emulsions of natural and synthetic rubber latices.   Richardson[12] used oil-in-water emulsions of benzene emulsified with sodium oleate.   Sibree[13,14] used oil-in-water emulsions of limpid and viscous paraffins emulsified with sodium oleate.   Simpson[15] used nitrocellulose lacquer emulsions emulsified with sodium polyvinylacetate phthalate.   Traxler, Schweyer and Romberg[16] determined the viscosity of asphalts processed by different methods.

The viscosity curves of all these workers show shear-rate thinning. Following the example of Hatschek, each of the authors has taken the limiting viscosity, i.e., the viscosity at infinite rate of shear, as a characteristic of the emulsion.   It is shown in Figure 2 that the curves A and B have the same limiting viscosity, but they have quite different consistencies. It is important to realise that the limiting viscosity alone is insufficient to
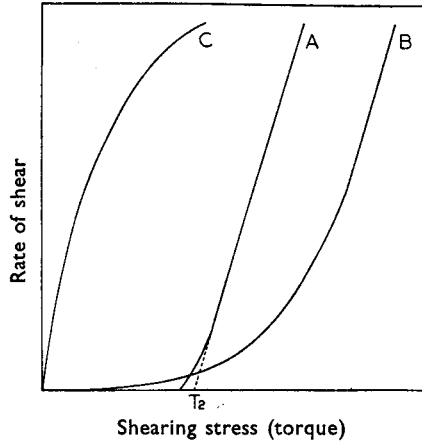
characterise systems which show shear-rate thinning. The entire viscosity curve is required.

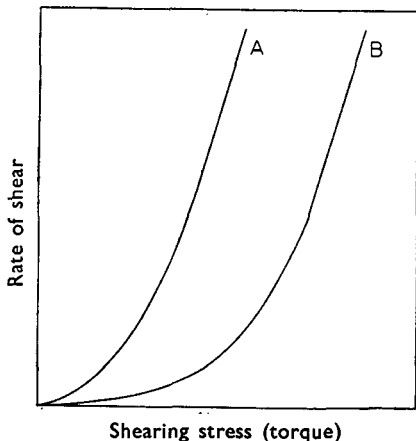Some of the above workers[10] have extrapolated the limiting viscosity curve at infinite rate of shear to the shearing stress (torque) axis, and designated this as a yield value which would suggest plastic flow. It would appear, however, as Sumner[17] has pointed out, that "Although very concentrated emulsions have a stiff consistency, quantitative evidence of *plastic* behaviour appears to be lacking." The author has been unable to find any conclusive evidence in the literature of an emulsion showing either uniform plastic flow or shear-rate thickening.

Fig. 2. Viscosity curves typical of preparations showing shear-rate thinning.

Choice of instrument. There are 2 main groups of instruments which give complete viscosity curves, viz., concentric cylinder rotational viscometers and mobilometers. To obtain a complete viscosity curve was a long and tedious procedure with the early instruments. The incorporation of a variable speed drive in the rotational viscometer[4,5] has made it possible for the two complete viscosity curves as described in this paper to be determined in 3 minutes. A permanent graphical record of the flow properties of semi-solid preparations can be obtained in a reasonable time in place of the rather unsatisfactory "single-point" determinations of consistency. This instrument developed by Green[4,5] illustrates experimentally the theories advanced by Bingham[18] and mathematically formulated by Reiner and Riwlin[19,20]. A viscosity curve is obtained in which rate of shear and torque are calculated from the dimensions of the instrument and are expressed in basic fundamental units which are independent of the instrument and of the observer. Briefly, the viscosity curve consists of an upcurve showing the effect of the increasing rates of shear and a downcurve to retrace the path as the rate of shear is reduced. The upcurve is obtained by plotting the deflection at each point when the speed of the cup is increased step by step. At 100 r.p.m. and 200 r.p.m. the speed of the cup is decreased and the deflections again recorded. The changes are made without stopping the rotation of the cup and are spaced as evenly as possible both in regard to speed of the cup and time interval. The Reiner and Riwlin equation is applied for calculation of the results.

The Reiner and Riwlin equation

$$\Omega = \left(\frac{T}{4 \times \pi \times h \times U}\right)\left(\frac{1}{R_b{}^2} - \frac{1}{R_c{}^2}\right) - \left(\frac{f}{U}\right)\ln\frac{R_c}{R_b} \quad Equation\ 1$$

can be separated conveniently into equations for

$$U = \frac{\left(T - T_2\right)9 \cdot 55\left(\dfrac{1}{R_b{}^2} - \dfrac{1}{R_c{}^2}\right)}{4 \times \pi \times h \times (\text{r.p.m.})} \quad .. \quad .. \quad \textit{Equation 2}$$

$U = T - T_2$ in degrees $\times k \times 9 \cdot 55 \times 0 \cdot 001844$
$U =$ Slope in degrees $\times 0 \cdot 05019$ *poises*

$$\text{and} \quad f = T_2\left[\frac{\dfrac{1}{R_b{}^2} - \dfrac{1}{R_c{}^2}}{4 \times \pi \times h \times \ln\dfrac{R_c}{R_b}}\right] \quad .. \quad .. \quad .. \quad \textit{Equation 3}$$

$f =$ intercept on the torque axis in degrees $\times k \times 0 \cdot 01618$.
$f =$ intercept in degrees $\times 4 \cdot 610$ *dynes per sq. cm.*
where $U =$ "plastic viscosity" in poises.
$f =$ yield value in dynes per sq. cm.
$\Omega =$ angular velocity in reciprocal seconds.
$T =$ torque in dyne cm.
$T_2 =$ intercept on the torque axis.
$R_b =$ radius of bob   .. $1 \cdot 300$ cm.
$R_c =$ radius of cup   .. $1 \cdot 457$ cm.
$h =$ height of bob   .. $5 \cdot 203$ cm.
$k =$ spring constant   .. 285.

The rate of shear at 100 r.p.m. is $45 \cdot 7$ reciprocal seconds and at 200 r.p.m. $91 \cdot 4$ reciprocal seconds.

The "plastic viscosity" U has dimensions M/LT the same as the coefficient of viscosity (Newtonian).

The yield value has dimensions M/LT^2.

For a preparation which shows shear-rate thinning, the limiting viscosity at infinite rate of shear is calculated by multiplying the slope of the down-curve by the "U" factor. The whole curve expressed in fundamental units is necessary, however, to characterise the system rheologically.

For a preparation which shows uniform plastic flow, the two values "plastic viscosity" and yield value are calculated; the "plastic viscosity" by multiplying the slope of the downcurve by the "U" factor, the yield value by multiplying the intercept on the torque axis (T_2) by the "f" factor. These two criteria are sufficient to describe the rheological properties of the preparation.

EXPERIMENTAL

Preparation of Emulsions. Emulsions were prepared to the following formulae:—

	I	II
Liquid paraffin B.P. ..	25·0 g.	25·0 g.
Emulsifying wax B.P. ..	5·0 g.	5·0 g.
Bentonite B.P.	0·0 g.	2·0 g.
Distilled water B.P. to ..	100·0 g.	100·0 g.

Method A. The emulsifying wax was melted in the liquid paraffin by heating in a water bath maintained at 70° C. The aqueous phase, also at 70° C., was added to the oil phase. The emulsion was then formed by homogenisation for 2 one-minute periods separated by a half-minute interval.

Method B. An emulsion was prepared by Method A using formula I, but making the total weight 80 g. While the emulsion was still at 70° C., it was diluted with distilled water and bentonite suspension also at 70° C., to produce formula I and II respectively.

Method C. An emulsion was prepared by Method A using formula I, but making the total weight 80 g. When the emulsion had cooled to room temperature, it was diluted with distilled water and bentonite suspension, also at room temperature, to produce formulae I and II respectively.

The emulsions were then packed in screw-capped ointment jars and sealed with an efficient white rubber wad closure.

Heat treatment of the emulsions. The jars of the different emulsions were then subjected to various heat treatments so that a comparative study of the change in consistency could be made.

Heating to 70° C. or 75° C. The jars of emulsion were immersed for 30 minutes in a thermostatically controlled water bath.

Heating to 100° C. This process was carried out by free steaming in an autoclave for 30 minutes.

Heating to 115° C. The jars of emulsion were autoclaved at 115° C. for 30 minutes.

Storage. All the emulsions were maintained at room temperature prior to viscosity determinations.

Determination of the viscosity curve. The emulsion was transferred from the jar to the cup of the viscometer which was placed in position in the water bath. The bob was slowly moved into the emulsion until the top of the bob was level with the top of the cup. When the emulsion and bob reached 25° C., the temperature at which all determinations were made, the surface was smoothed level with the top of the cup and the viscosity determined.

For the first viscosity curve, readings of the deflection of the bob were taken as the speed of the cup was increased by intervals of 10 r.p.m. until 100 r.p.m. was reached and again as the speed was decreased step by step to 0 r.p.m.

The second viscosity curve was started at 100 r.p.m. and readings taken at 20 r.p.m. intervals up to 200 r.p.m., when the speed was reduced step by step to 40 r.p.m., and then by 10 r.p.m. intervals to 0 r.p.m.

The deflection in degrees was then plotted against the speed of the cup and a straight line was drawn through the maximum number of points on the downcurve and extrapolated to cut the torque axis.

Typical viscosity curves for heated emulsions prepared to formula I and II are shown in Figures 3, 4, 5, and 6.
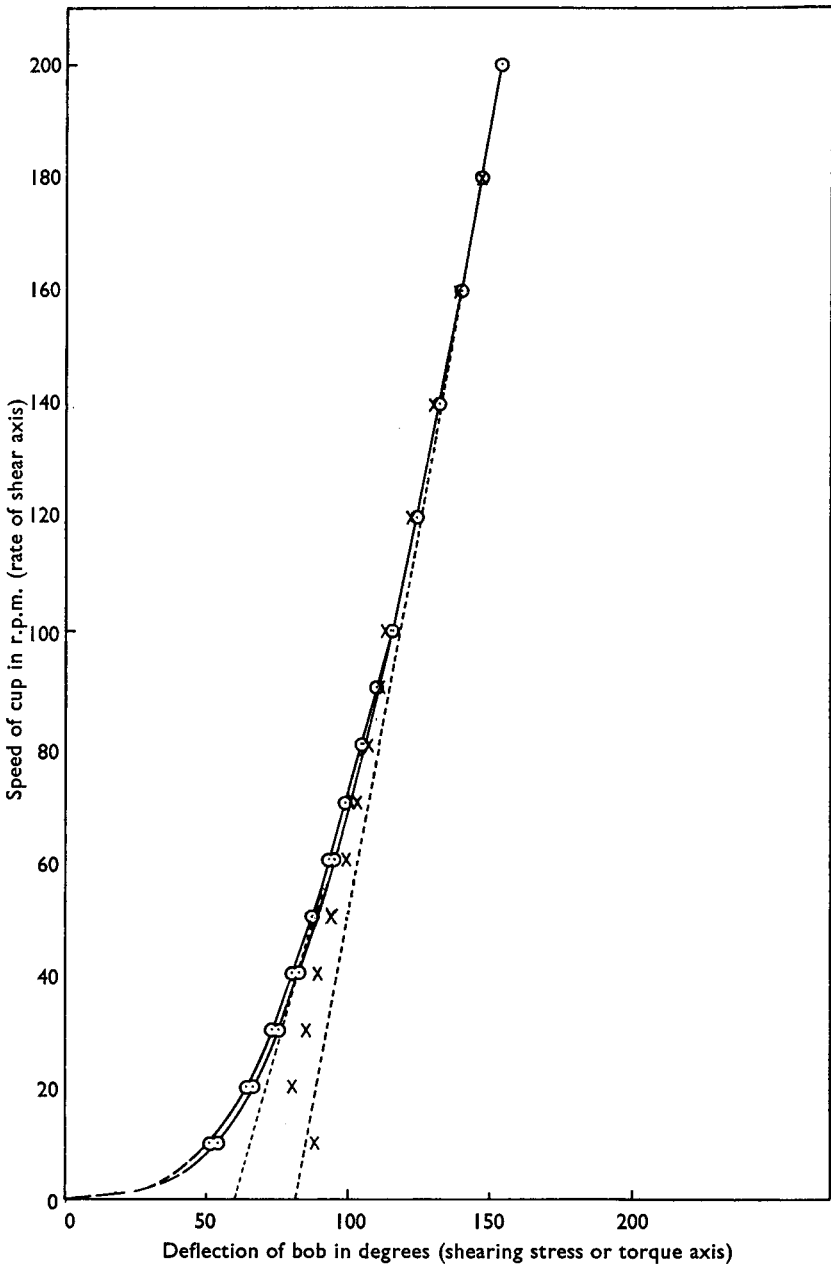
FIG. 3. Emulsion prepared without bentonite heated to 75° C.   D.I. 75° C.   No. 97.

⊙————————⊙   Downcurve.
×   Points on upcurve.
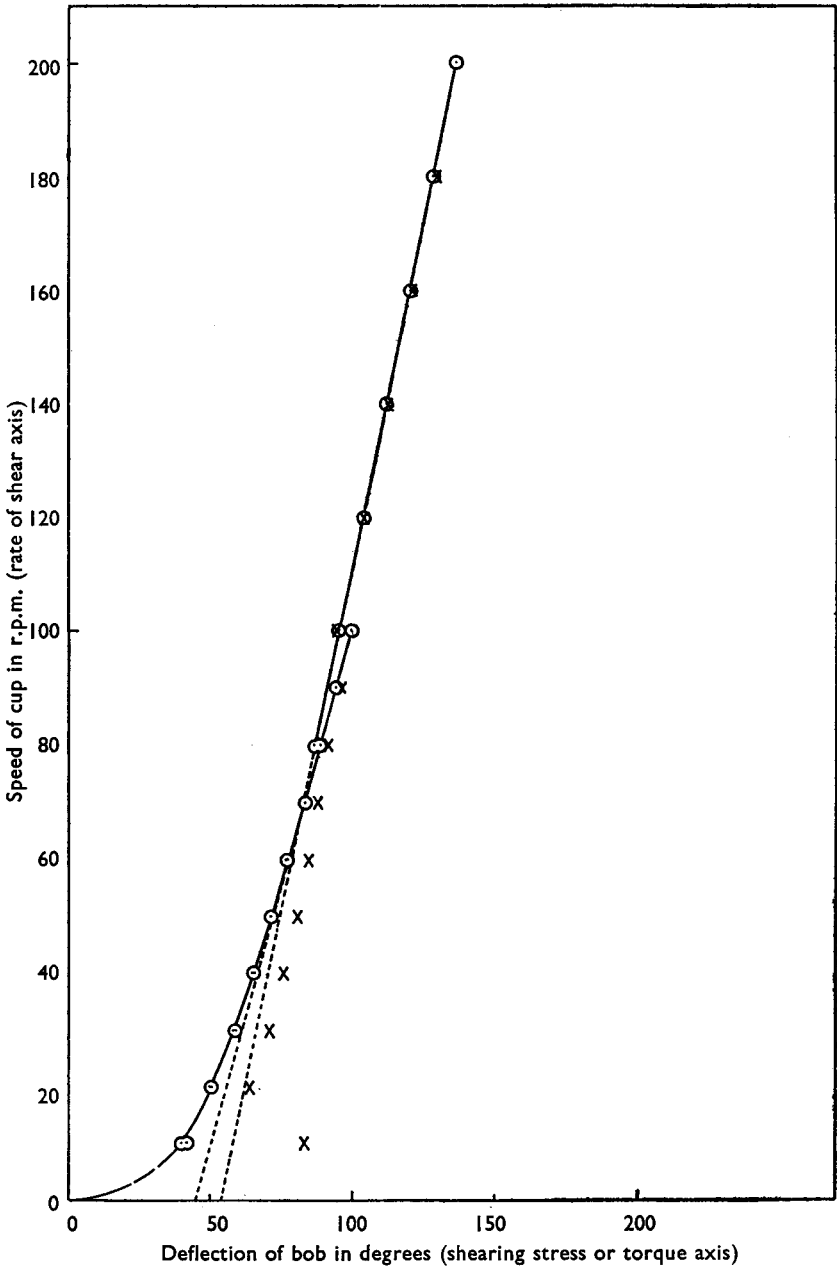— — — — —   Extrapolation of rectilinear part of curve
to the torque axis.

FIG. 4. Autoclaved emulsion prepared without bentonite D.I.A. No. 122.

⊙————⊙ Downcurve.
× Points on upcurve.
— — — — — Extrapolation of rectilinear part of curve
to the torque axis.
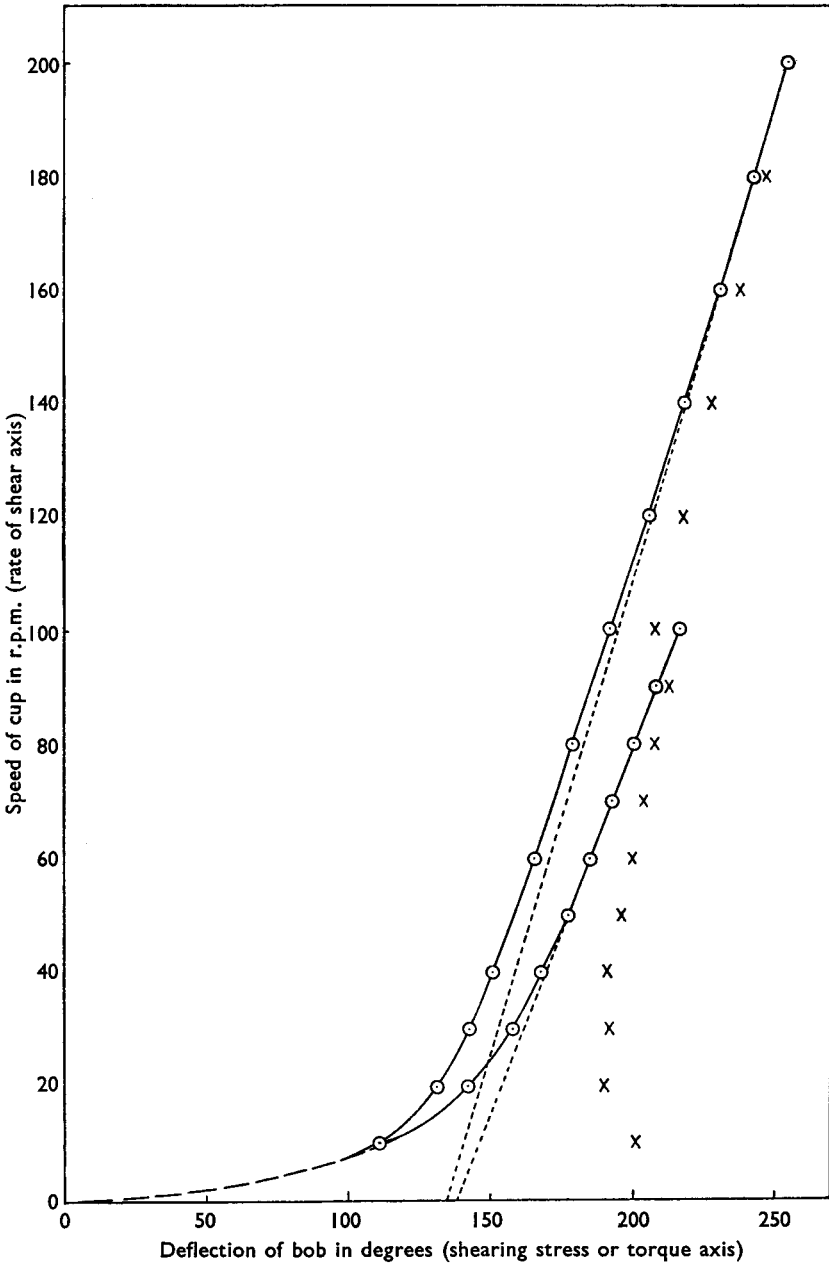
FIG. 5. Emulsion containing bentonite heated to 70° C. E.II.70° C. No. 116.

⊙————⊙ Downcurve.
× Points on upcurve.
— — — — — Extrapolation of rectilinear part of curve
to the torque axis.

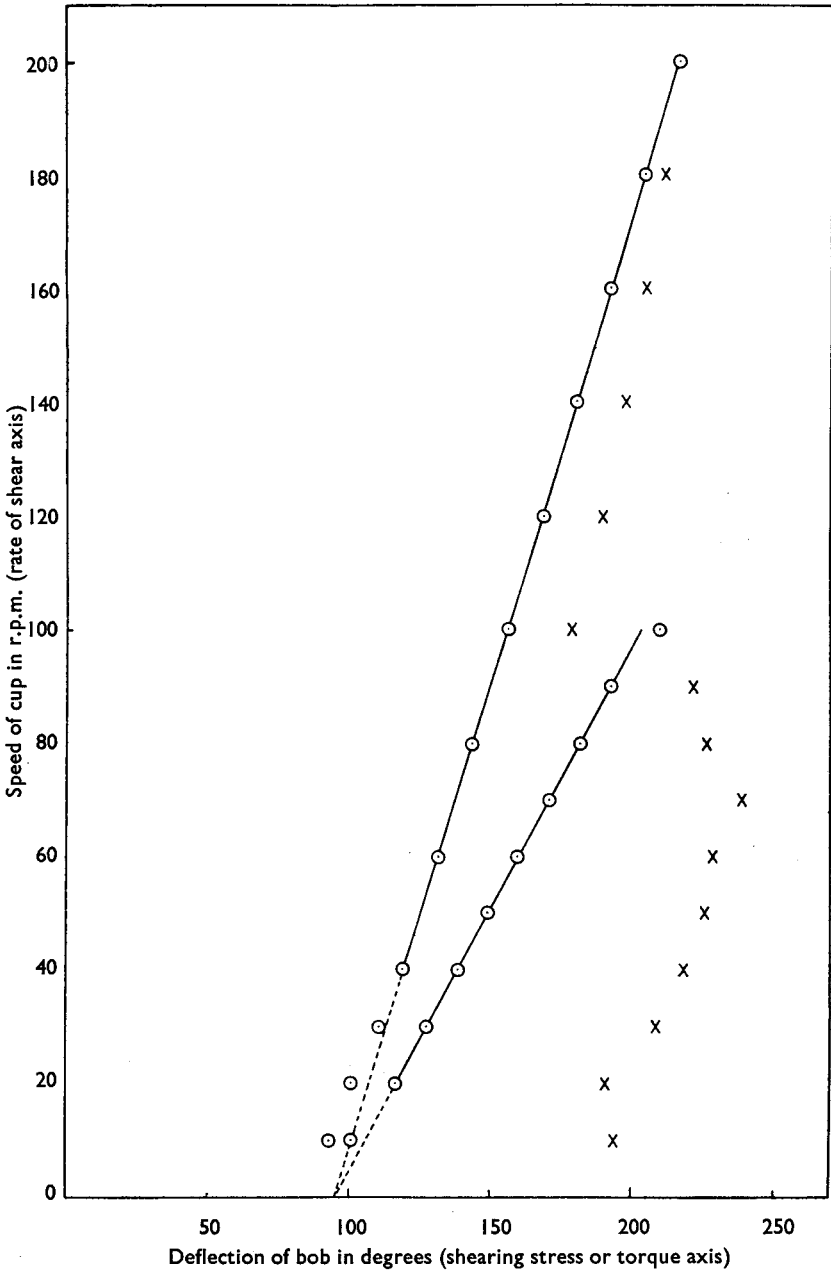FIG. 6.   Autoclaved emulsion containing bentonite E.II.A.   No. 134.

⊙————⊙   Downcurve.
×   Points on upcurve.
— — — — —   Extrapolation of rectilinear part of curve
to the torque axis.

INTERPRETATION OF THE RESULTS OF THE VISCOSITY DETERMINATIONS

(1) *Emulsions prepared without bentonite (Formula I)*

Emulsions without bentonite have been prepared by each of the methods A, B, and C.

Untreated emulsions. Emulsions which have not been subjected to any heat treatment after preparation show shear-rate thinning.

Emulsions heated to 70° C., 75° C., or 100° C. Emulsions which have been heated to temperatures of 70° C., 75° C., and 100° C. show shear-rate thinning.

Emulsions heated to 115° C. Emulsions which have been autoclaved at 115° C. show shear-rate thinning.

The viscosity determinations show a downcurve which is rectilinear only for the uppermost portion of the downcurve. At low rates of shear the curves appear to pass through the origin. The entire viscosity curve is necessary to characterise the emulsion consistency. For all the emulsions prepared without bentonite the downcurves are not coincident with the upcurves, which indicates that some thixotropic breakdown has occurred on shearing.

(2) *Emulsions containing bentonite (Formula II)*

Emulsions containing bentonite have been prepared by each of the methods A, B, and C.

Untreated emulsions. Emulsions which have not been subjected to any heat treatment after preparation show shear-rate thinning.

Emulsions heated to 70° C., 75° C., and 100° C. Emulsions which have been heated to temperatures of 70° C., 75° C., and 100° C., show shear-rate thinning.

The above emulsions are characterised by a downcurve which is rectilinear only for the higher rates of shear. At low rates of shear the curves appear to pass through the origin. The entire viscosity curve is necessary to characterise the emulsion consistency.

Emulsions heated to 115° C. The viscosity determinations show that the autoclaved emulsions exhibit uniform plastic flow. They are characterised by a downcurve from 100 r.p.m. which is rectilinear above 10 r.p.m., and a downcurve from 200 r.p.m. which is rectilinear above 40 r.p.m. The curves meet at a common value of T_2, which indicates that the yield value is independent of the rate of shear and of the time of shear.

For all the emulsions prepared with bentonite the downcurves are not coincident with the upcurves, which indicates that some thixotropic breakdown has occurred on shearing.

The viscosity determinations for autoclaved emulsions prepared without bentonite are shown in Table I; those for autoclaved emulsions containing bentonite are shown in Table II.

CONCLUSIONS

Autoclaved emulsions prepared without bentonite

Emulsions which have been prepared by Method A, which is current practice in the pharmaceutical industry, show a satisfactory reproducibility.

TABLE I

Autoclaved Emulsions Prepared Without Bentonite

Cream	Method of preparation	Number	Storage days	Point of intersect on torque axis, dynes/sq. cm.		Viscosity at 25° C. poises	
				100 r.p.m.	200 r.p.m.	lim→ 100 r.p.m.	lim→ 200 r.p.m.
J.I.A.	A	169	2	396·5	359·6	5·02	2·51
		183	7	355·0	368·8	4·47	2·48
		230	21	387·2	368·8	4·37	2·56
		309	64	391·8	368·8	4·17	2·53
U.I.A.	A	303	0	442·6	401·1	4·32	2·23
		308	1	396·5	364·2	4·27	2·16
		317	4	368·8	350·4	3·81	1·86
		336	29	318·1	304·3	4·57	2·31
D.I.A.	B	104	2	258·2	322·7	3·26	2·28
		122	8	207·4	253·5	2·76	2·06
		179	29	175·2	225·9	2·46	1·91
		310	102	170·6	221·3	2·26	1·76
E.I.A.	B	114	2	461·0	433·3	4·67	2·71
		226	37	281·2	262·8	3·46	1·83
		311	85	355·0	359·6	4·72	2·28
		337	113	355·0	350·4	4·92	2·33
G.I.A.	C	168	2	405·7	373·4	5·37	2·48
		182	7	414·9	437·9	4·37	2·56
		227	16	368·8	355·0	3·91	2·58
		314	65	396·5	396·5	4·12	2·46
O.I.A.	C	214	1	387·2	364·2	4·12	2·33
		216	4	341·1	368·8	4·27	2·53
		229	11	322·7	350·4	4·22	2·53
		315	55	318·1	341·1	3·81	2·48

TABLE II

Autoclaved Emulsions Containing Bentonite

Cream	Method of preparation	Number	Storage days	Yield value at 25° C. dynes/sq. cm.	"Plastic viscosity" at 25° C. poises	
				f_{100} and f_{200}	U_{100}	U_{200}
B.II.A	A	105	29	461·0	6·22	3·26
		157	48	442·6	5·87	3·11
		192	60	470·2	5·62	3·11
		319	121	451·8	5·62	3·01
H.II.A	A	175	3	447·2	4·97	2·96
		188	7	442·6	5·82	3·09
		320	67	461·0	6·47	3·21
		339	92	461·0	6·02	3·16
D.II.A	B	93	12	433·3	5·82	2·86
		144	31	442·6	6·02	2·79
		213	49	451·8	5·82	2·61
		321	105	433·3	6·02	2·63
E.II.A	B	115	2	451·8	5·77	2·96
		134	9	442·6	5·42	3·04
		146	15	451·8	5·87	3·09
		322	88	470·2	5·77	2·89
G.II.A	C	167	2	414·9	5·82	2·91
		181	4	433·3	5·82	3·11
		193	8	461·0	5·52	3·11
		323	67	447·2	5·67	3·04
N.II.A	C	219	4	442·6	5·42	3·11
		220	4	447·2	5·37	2·94
		325	57	451·8	5·32	3·01
		338	72	470·2	5·62	3·06

The entire viscosity curve is necessary fully to characterise the emulsion. Emulsions prepared by Method C, which is the dilution of a more concentrated emulsion at room temperature, also give results which are reproducible and comparable with those made by Method A. The emulsions prepared by Method B, which is the dilution of a more concentrated emulsion at 70° C., do not show the same reproducibility, and there appears to be some thinning on storage. All the emulsions show some evidence of thixotropic breakdown.

Autoclaved emulsions containing bentonite

Emulsions, whether prepared by Methods A, B, or C, show a satisfactory reproducibility after autoclaving. All the emulsions show some evidence of thixotropic breakdown which is generally greater than that shown by emulsions prepared without bentonite. They can be characterised by the two factors:—

1. The "plastic viscosity":—at 45·7 reciprocal seconds (100 r.p.m.) of 4·97 to 6.47 poises; at 91·4 reciprocal seconds (200 r.p.m.) of 2·61 to 3·26 poises.
2. The yield value, which varies between 415 and 470 dynes per sq. cm.

SUMMARY

1. The rotational viscometer having a variable speed drive can be used to give a viscosity curve expressed in fundamental units.
2. Two viscosity curves which will characterise the consistency of a pharmaceutical cream base, at a given temperature, can be obtained in a reasonable time for control purposes.
3. The consistency of autoclaved emulsions prepared with and without bentonite has been determined quantitatively and the results tabulated.
4. Emulsions prepared without bentonite showed shear-rate thinning both before and after autoclaving.
5. A change in type of viscosity from shear-rate thinning to uniform plastic flow occurred when an emulsion containing bentonite was autoclaved.
6. The entire viscosity curve is necessary to characterise shear-rate thinning whereas uniform plastic flow can be characterised by two factors: "plastic viscosity" and yield value.

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DISCUSSION

The paper was presented by THE AUTHOR.

The CHAIRMAN, in introducing the discussion, said that bentonite was a peculiar substance, and if methods could be devised to amend the standards and so ensure greater uniformity in B.P. material it would be a great help.

MR. S. G. E. STEVENS (London) said experience showed that merely to prepare a suspension with a water basis and to measure empirical viscosity tended to be misleading. The present specifications for bentonite were insufficient. He had insisted that all material should be delivered from one mine in America, which was the only way to achieve uniformity of product. In addition, his specification included his own viscosity test.

MR. A. W. BULL (Nottingham) emphasised the material differences which occurred in bentonites which complied with B.P. requirements. His colleagues had published work on calamine lotion using bentonites from different sources, and it had been found that the genuine Wyoming bentonite was the most constant product.

MR. AXON, in reply, said that figures for apparent viscosity and empirical viscosity were meaningless. The viscometer used must be able to give rates of shear and shearing stresses in absolute units. Without that, little could be achieved with substances which exhibited anomalous viscosities.