

Some Aspects of PVC Paste Rheology

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Synopsis

Using the Weissenberg rheogoniometer, a technique has been developed which facilitates the measurement of shear stress data and which substantially overcomes the problem of sample loss that normally occurs at high shear rates. Using this technique, the apparent viscosities of PVC pastes based upon four different PVC paste polymers plasticized with dialkyl phthalate have been determined at a number of shear rates up to 9000 sec^{-1} and the viscosity aging characteristics of these paste polymers have been compared. The effect of several common plasticizers upon PVC paste viscosity and viscosity aging have been studied at shear rates of the order of 10 sec^{-1} and 1000 sec^{-1} .

INTRODUCTION

PVC paste polymer is normally polymerized using an emulsion process. It differs from PVC suspension and mass polymers which are used in extrusion, injection and blow molding, etc., mainly in terms of particle size and structure. For example paste polymer consists of particles whose diameters lie between 0.5 and 2.0 microns, whereas suspension polymer has particles which are a hundred times as large. These differences significantly alter the behavior of the polymer when mixed with a plasticizer at room temperature. A PVC paste consists of a mixture of paste polymer, plasticizer, and other additives which may include stabilizer, filler, pigment, viscosity modifier, organic solvent, and blowing agent, and the consistency of the paste can range from a thin cream to a thick gel. It is normally prepared by mixing the constituents at room temperature in a Z-blade or planetary mixer, and vacuum is usually applied during or after mixing to minimize air entrapment.

Pastes are processed by a variety of techniques including spreading, dipping, spraying, rotational casting, and slush molding. In all of these processes, the paste is applied to the substrate or mold at room temperature and is subsequently fused by heating to temperatures of the order of 180°C. The rheological characteristics of a paste will significantly affect its processing characteristics, and viscosity control is always an important feature of paste processing. In particular, some of the more recent sophisticated processes such as high-speed paper coating impose stringent requirements upon the viscosity and other rheological properties of the paste. It is surprising therefore that so little has been published concerning the relation-

ships between paste rheology and processing, and thus the subject is fraught with misconceptions. The paste technologist frequently confuses terms such as thixotropy and pseudoplasticity, which we shall define below. Few paste technologists have at their disposal the facilities for relevant viscosity measurement, and perhaps this is why PVC paste technology remains in some respects an art rather than a science.

THEORETICAL DISCUSSION

PVC Pastes

Rheological studies usually involve the determination of shear rate and shear stress relationships and the calculation of apparent viscosities.

The "shear stress" can best be described with reference to an elemental cube which is illustrated in Figure 1b. The force $P(zx)$, which is depicted there, is a force acting along the face ABCD in the direction Ox . In the case of an element with curved faces the shear stresses become the tangential stresses and act along the tangents at any point. The "shear rate" describes the change in shape of this element due to this shearing force.

In the case of simple shear, the shear rate will be equal to the velocity gradient in the fluid under test (Fig. 1a). However, it should be pointed out that this is only true for certain types of shear flow. If we consider the

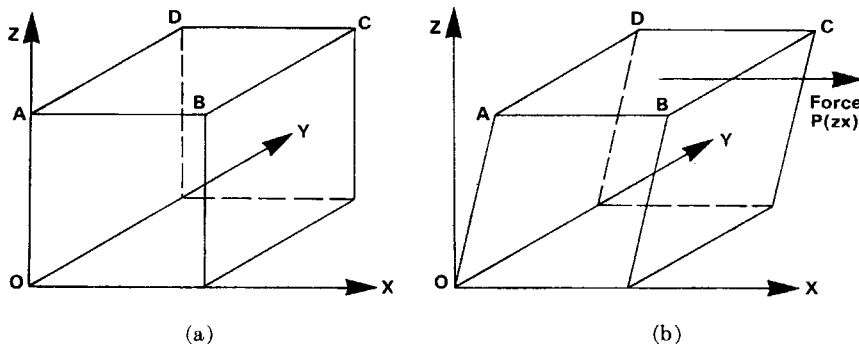


Fig. 1. (a) Element not subject to any shearing force. (b) Element subjected to a simple shearing force causing deformation of element.

case of a cone-and-plate viscometer with fluid filling the gap between the cone and the plate, then a state of unidirectional shear flow will exist for constant rotational speed of the cone. In this case it is quite valid to take the velocity gradient as the shear rate, and it can easily be seen to be a linear function of the rotational speed of the cone. The shear stress will be a simple function of the torque experienced by the plate during testing. The apparent viscosity will be the ratio of the shear stress to the shear rate.

In the following sections we shall discuss some of the different types of shear stress/shear rate relationships which are exhibited by fluids.

Newtonian Fluids

A Newtonian fluid has an equation of state in which the shear rate and shear stress are directly proportional and are related as follows:

$$\tau = \eta \dot{\gamma}$$

where τ is the shear stress, $\dot{\gamma}$ the shear rate, and η is a constant. The constant η is known as the viscosity coefficient.

Dilatancy and Pseudoplasticity

Fluids in which the ratio of the shear stress to the shear rate vary with the shear rate are known as non-Newtonian fluids. These may exhibit pseudoplasticity in which this ratio, known as the apparent viscosity, will decrease with increasing shear rate. The converse effect is known as dilatancy, and this will give rise to increasing apparent viscosity with increasing shear rate. These two phenomena are illustrated in Figure 2a and 2b.

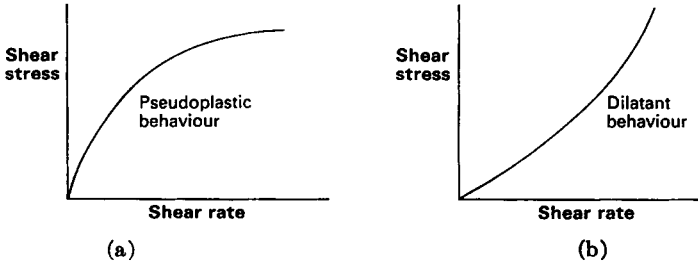


Fig. 2. (a) Pseudoplasticity; (b) dilatancy.

It would be convenient from a theoretical standpoint if we could characterize these materials by a simple analytical equation of state. A power law is frequently used and this is given by

$$\frac{\eta}{\eta_0} = \left(\frac{\dot{\gamma}}{\dot{\gamma}_0} \right)^{n-1}$$

where η is the apparent viscosity of the material when the shear rate is $\dot{\gamma}$. $\dot{\gamma}_0$, η_0 are, respectively, the corresponding shear rate and apparent viscosity at some reference point; $\dot{\gamma}_0$ is frequently taken as 1 sec^{-1} , and η_0 will then be the viscosity at this shear rate. The index n , which will be greater than unity for a dilatant material and less than unity for a pseudoplastic one, can be determined experimentally. However, even though some materials do appear to obey such a law for limited ranges of shear rate, it must be remembered that this is a purely empirical equation. It is not based on any theory of fluid dynamics and is therefore not a general result. For the purpose of theoretical calculations, it can be used within the shear rate range in which it has been proved experimentally. However, extrapolating outside this range by means of such an equation would give results of no value.

Bingham Plastic

Fluids which appear to obey the equation of state given by

$$\tau = \eta\dot{\gamma} + S$$

where S is some arbitrary constant, are known as Bingham bodies. Before this type of material will flow or deform, an initial finite stress must be applied which is then known as a yield value. However, it has been suggested that a small region of very high viscosity exists at very low shear

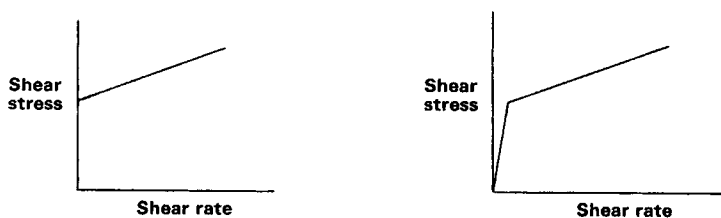


Fig. 3. Bingham behavior.

rate, and at some point this viscosity will suddenly start decreasing rapidly over another small shear rate region. This, in fact, has been borne out by some experiments performed by the authors on a sample of printing ink. These two theories are illustrated by Figures 3a and 3b.

Thixotropy and Rheopexy

A reduction in shear stress with time for a fluid sample subjected to a constant rate of shear is known as thixotropy (see Fig. 4a). This is thought to be due to the breaking down of internal structuring which is present in the paste at rest. If, after shearing, the sample is allowed to rest, then on repeating the test the same initial shear stress should be achieved. This structuring is therefore recoverable.

If, on the other hand, the fluid sample becomes more viscous with time at constant shear rate, then this is called rheopexy (see Fig. 4b).

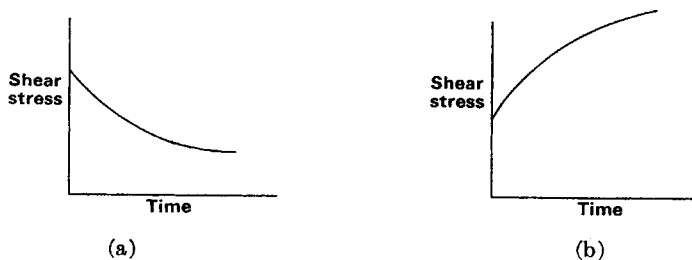


Fig. 4. (a) Thixotropy; (b) rheopexy.

PRACTICAL CONSIDERATIONS

Aging

A PVC paste is a dispersion of polymer in plasticizer, and the effect of the plasticizer is to swell the polymer resulting in an increase in the fraction of the total volume occupied by the solid particles. The compatibility of the polymer with its plasticizer will control the rate at which this swelling of the polymer occurs, and the effect is an increase in viscosity. Thus, the viscosity of a paste shows an aging effect which normally takes several days to achieve completion.

Now, pastes are not always processed within a few hours of mixing, and when the paste has not been prepared by the processor but has been bought in, it may be several weeks old at the time of processing. The viscosity aging characteristics of a paste are therefore of prime importance to the processor.

Effect Upon Processing

The anomalous flow properties of a PVC paste significantly affect its processing characteristics and can cause serious problems.

A paste which is dilatant at high shear rates can give rise to uneven thickness during high-speed coating due, for example, to variations in tension, causing the shear rate, and hence the viscosity, to vary; this process requires pseudoplasticity at high shear rates. On the other hand, a paste which is highly viscous at very low shear rates would be suitable for dipping where this property would prevent dripping. A problem frequently encountered during spreading is one of strike-through when coating an open weave fabric; this can be inhibited by a high viscosity at low shear rates, by a high yield value, and by thixotropy.

VISCOMETERS

There is a wide range of different types of viscometers used by PVC paste technologists; these are best considered under the following three headings:

1. Simple viscometers such as the Brookfield and the Ford Cup system are widely used as quality control instruments by the processor. These can be of considerable value as quality control instruments, but they cannot be used to obtain shear rate/shear stress data. The Brookfield is probably the most popular of these simple instruments and is based upon the rotation of a spindle in the paste; the shear rate varies at different points on the spindle and therefore cannot be expressed in terms of a single value.

2. Capillary and extrusion viscometers such as the Instron capillary attachment and the Severs viscometer can be used to obtain shear rate/shear stress data. These instruments involve the extrusion of the paste from a capillary or barrel through a nozzle of known dimensions by means of a plunger or gas pressure. With this type of viscometer, the calculation to

obtain a value for the shear rate on the wall usually involves a number of correction factors. In the determination of these factors, the assumption is made that the fluid obeys one of the simple equations of state, and this is certainly false when dealing with PVC pastes. Even if such an equation of state was applicable, the errors of measurement listed by Van Wazer and co-workers¹ which have to be corrected for, make this type of system unsuitable for work in which vast quantities of data are required. For measurements at very high shear rate, e.g., of the order of 6,000 to 10,000 sec⁻¹, either the pressure would have to be very large or the nozzle diameter extremely small, and, in either case, extrusion of a viscous material under such conditions would be very difficult, particularly in the case of a dilatant material.

3. Thirdly, there are rotational viscosimeters such as the Ferranti-Shirley, the Rotovisco, and the Weissenberg rheogoniometer. The Ferranti-Shirley has only a cone and plate. However, the other two viscosimeters have concentric cylinder attachments. In both these configurations the test sample is placed in the gap between the cone and plate or between the concentric cylinders. One member is rotated at some known speed while the other is kept stationary. The advantage of this type of viscosimeter is that the shear rate is constant along the surface where the shear stress is measured. The shear stress is found by measuring the torque on one of the shearing surfaces, and hence the apparent viscosity is readily calculated. Pastes are usually elasticoviscous fluids, and the combined effect of the normal forces generated in the fluid under shear together with the forces due to the rotational action of the viscosimeter will cause sample loss in the case of cone-and-plate and concentric cylinder-type viscosimeters. This sample loss effect does not occur at very low shear rates, but unambiguous rheological data is difficult to achieve with viscosimeters of these types at high shear rate. This paper explains how the sample loss effect has been substantially overcome using the Weissenberg rheogoniometer.

EXPERIMENTAL

Initial work carried out using the Ferranti-Shirley viscosimeter had indicated that sample loss can occur to a limited extent at all shear rates. For a typical paste, this is not normally significant below 100 sec⁻¹. Therefore, it had not been possible to obtain unambiguous shear rate/shear stress data at high shear rates.

To overcome this problem, the work described in this paper was carried out using the Weissenberg rheogoniometer. This instrument is a cone-and-plate viscosimeter. The cone is positioned on the lower platen and the plate, on the upper platen, and it is the lower platen which rotates. The 1-HP motor has a maximum speed of 3000 rpm, and the gear box is designed to give 60 different rotational speeds. The clutch mechanism can transmit power from the motor to the lower platen almost instantaneously, so that on engaging the clutch, the time taken for the cone to accelerate from zero to the required speed is small enough to be disregarded. The

stationary platen is attached via a frictionless air bearing to the bottom of a torsion bar which is rigidly clamped at the top. The shear stress experienced by the stationary platen when the cone rotates is transmitted to the torsion bar which twists accordingly, and this effect is measured by a transducer and recorded on a dial.

For the purposes of this work, it was important to obtain an instantaneous reading of the shear stress before the onset of sample loss. A fast recording method was necessary for which a pen recorder was too slow. For this purpose, the signal from the torsion head transducer was diverted into a UV recorder, and this gave a trace of a function of shear stress versus time. The absolute shear stress in dynes per cm^2 was readily calculated from the UV trace, the constant of conversion being dependent upon the choice of torsion bar and on the platen diameter.

The absolute shear rate in reciprocal seconds was readily calculated, this being a function of the speed of rotation, the platen diameter, and the angle between the cone and plate. Having a knowledge of the shear rate and shear stress, the apparent viscosity of the paste under test was calculated.

Throughout the experiments herein described, the cone used had a diameter of 5 cm and an angle of 0.5 degrees. All the pastes were tested using a $1/4$ -in. torsion bar, and the viscosities of the plasticizers were measured using a $1/16$ -in. bar.

All the pastes described above were tested at shear rates of 11.38 sec^{-1} and 1138 sec^{-1} , and those based upon polymers A, B, C, and D were also tested at a range of shear rates up to 9020 sec^{-1} . All were tested after 1 and 14 days of aging at 23°C , and a number were also tested after 1 hr, 3 days, 7 days, and 21 days of aging.

TABLE I
PVC Paste Polymers

Polymer A	A speciality polymer suitable for high-viscosity applications only. The viscosity is too high for most spreading applications.
Polymer B	A general-purpose polymer, much more versatile than A, C or D. Performs well in normal and high-speed spreading and is less prone to give strike-through problems than C and D.
Polymer C	A specialty polymer suitable for medium/low viscosity applications. Is used in normal and high-speed spreading applications but is not particularly suitable for low-speed spreading where it gives rise to problems of uneven coating normally associated with dilatancy. Is more suitable for high-speed coating, but viscosity aging is regarded as a problem.
Polymer D	A speciality polymer suitable for very low-viscosity applications. Is superior to the other polymers in high-speed paper coating applications, and its viscosity aging is regarded as very good. Gives rise to severe strike-through problems relative to B when applied to an open weave.

Materials

Comparison of Polymers. The PVC paste polymers involved in this comparison are given in Table I.

The formulation used was as simple as possible and consisted only of polymer and DAP plasticizer in the ratio of 100:60 by weight.

Comparison of Plasticizers. The plasticizers listed in Table III which are frequently used in PVC paste formulations were included in this investigation. Again, the formulation used was as simple as possible and consisted of polymer and plasticizer in the ratio of 100:70. The polymer used was

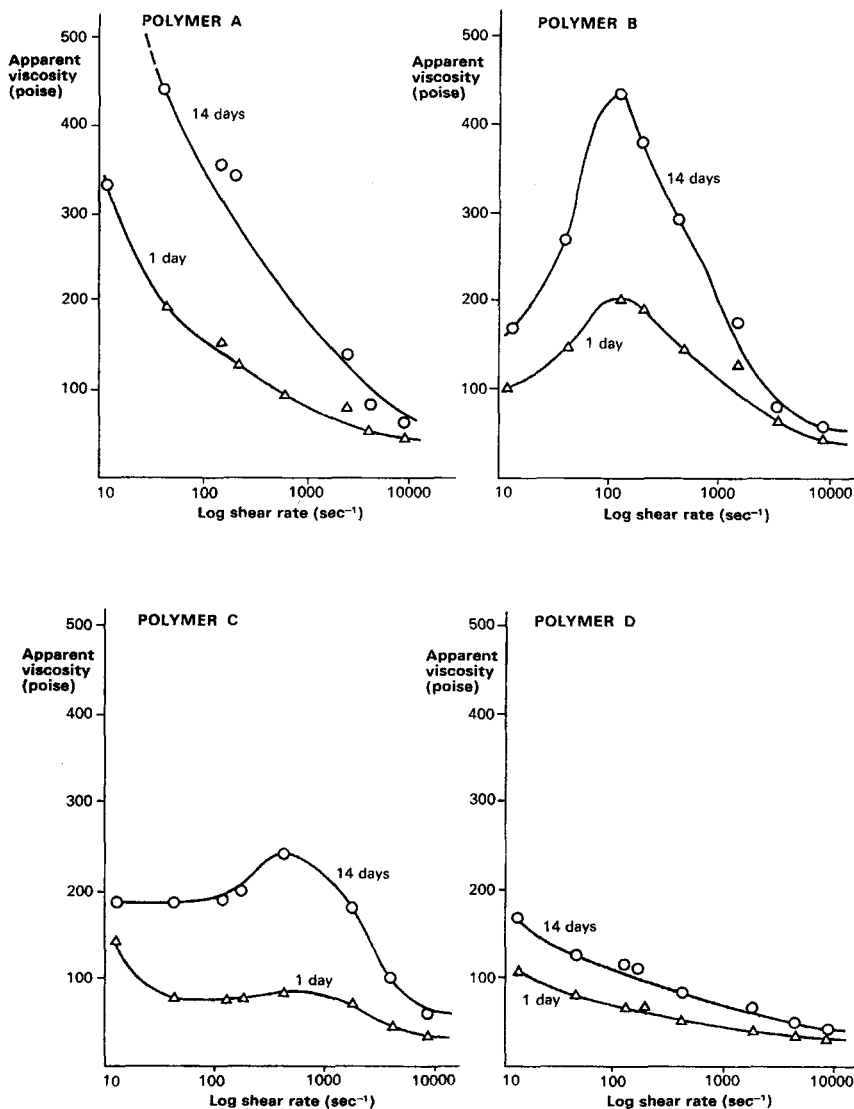


Fig. 5. Apparent viscosity/log shear after 1 and 14 days.

Breon P130/1, a general-purpose paste polymer manufactured by BP Chemicals (U.K.) Ltd.

Paste Preparation. The two constituents were weighed out and mixed by hand before being placed in a planetary mixer. A standard mixing procedure was adopted in each case. This involved mixing on a low-speed setting for 10 min to minimize aeration, after which time the sides of the bowl were scraped down to remove any free dry polymer; mixing was then continued for a further 10 min. Pastes were kept in an air-tight container and stored at 23°C.

RESULTS

Comparison of Polymers

The results obtained from the pastes based upon polymers A, B, C, and D are given in Table II and are represented graphically in Figures

TABLE II

Polymer	Shear rate, sec ⁻¹	Apparent viscosity, poises	
		1 day	14 days
A	11.38	332	948
	57	192	442
	114	150	356
	143	132	345
	570	92	205
	1434	83	138
	4522	53	84
	9020	38	64
	B	11.38	97
57		145	268
114		202	427
143		190	376
570		143	293
1434		126	176
4522		62	76
9020		42	48
C		11.38	146
	57	73	189
	114	73	193
	143	72	200
	570	78	247
	1434	67	182
	4522	44	99
	9020	32	60
	D	11.38	118
57		78	126
114		62	114
143		67	112
570		53	83
1434		48	69
4522		37	48
9020		29	33

TABLE III
Different Viscosities of Pastes

Plasticizer	Shear rate, sec ⁻¹	Apparent viscosity, poises						
		1 hr	1 day	3 days	7 days	14 days	21 days	
DAP, Dialkyl phthalate (phthalate of C ₇₋₉ alcohols normal branched, some cyclic)	11.38	28	40	55	76	67	104	
	1138	52	55	62	69	76	85	
DBP, Dibutyl phthalate	11.38	42	151	360	684	1740	3630	
	1138	54	130	226	366	726	845	
DIBP, Diisobutyl phthalate	11.38	34	68	88	164	225	296	
	1138	58	94	101	150	166	210	
DOP, Di-2-ethylhexyl phthalate	11.38	36	55	79	103	126	138	
	1138	54	49	78	70	77	79	
DIOP, Diisooctyl phthalate	11.38	30	71	99	115	95	99	
	1138	79	77	99	111	99	99	
DNP, Dinonylphthalate	11.38	28	43	40	46	70	63	
	1138	62	62	70	70	76	76	
DIDP, Diisodecyl phthalate	11.38	36	40	51	52	58	83	
	1138	76	73	81	84	76	79	
DTDP, Ditridecyl phthalate	11.38	75	71	73	75	88	92	
	1138	106	104	108	111	115	117	
Bisoflex ODN, Isooctyl isodecyl nylonate	11.38	8	8	12	12	12	12	
	1138	12	13	14	15	18	18	
DOA, Di-2-ethylhexyl adipate	11.38	6	12	13	14	20	17	
	1138	8	10	10	13	13	15	
DAA, Dialkyl adipate	11.38	8	13	28	27	35	41	
	1138	9	12	15	17	21	23	
Bisoflex L79P, Phthalate of the essentially linear C _{7-C₉} alcohols	11.38	20	29	38	54	71	86	
	1138	31	36	44	47	60	62	
Bisoflex L911P, Phthalate of the essentially linear C _{7-C₁₁} alcohols	11.38	20	32	36	39	43	43	
	1138	49	40	44	47	47	47	
BBP, Butylbenzyl phthalate	11.38	32	83	95	123	118	191	
	1138	198	265	308	358	356	420	
DCP, Dicapryl phthalate	11.38	28	32	44	54	60	67	
	1138	55	55	57	64	68	74	

5a, b, c, and d. These figures show the relationship between the apparent viscosity and the shear rate after 1 and 14 days of aging.

Comparison of Plasticizers

The apparent viscosities of the pastes based upon the various plasticizers are given in Table III.

DISCUSSION

Typical UV traces from the rheogoniometer UV recorder at 11.38 sec^{-1} , 1434 sec^{-1} , and 9020 sec^{-1} are shown in Figure 6. The decrease in shear stress with time observed at the higher shear rates was not recovered by arresting the application of shear for a period of about 5 min, and, therefore, this fall was due to sample loss and not to thixotropic breakdown.

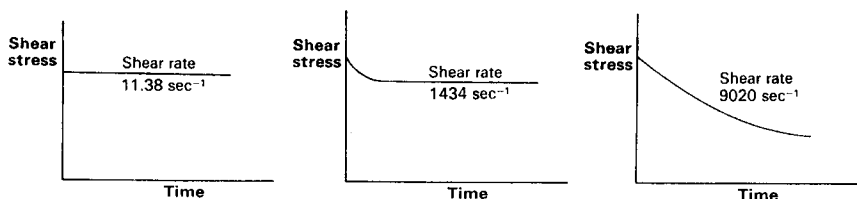


Fig. 6. Typical rheogoniometer for UV recorder traces.

The shear stress values used in the calculation of the apparent viscosities recorded in this paper were taken at zero time, and it has been assumed that these values were substantially unaffected by sample loss.

The rheological characteristics of the pastes based upon polymers A, B, C, and D are seen to be very different. Those pastes based upon polymers A and D show pseudoplasticity throughout the entire shear rate range, whereas the other two polymers show regions of dilatancy and pseudoplasticity.

It is interesting to speculate upon the importance of these very different rheological characteristics in relation to the known processing characteristics of the polymers, some of which are shown in Table I.

It is well known that a paste to be used in a spreading process needs to be pseudoplastic in the shear rate range relevant to the process since dilatancy gives rise to uneven coating and other production problems. Polymers B, C, and D are all pseudoplastic at high shear rates relevant to the high speed spreading process, and all are therefore suitable for this application. Polymer C is dilatant up to about 1000 sec^{-1} , and this would explain why this polymer sometimes gives problems in low-speed spreading applications where the relevant shear rate might be of the order of 1000

sec^{-1} . Polymer B is very dilatant at low shear rates which do not apply to most spreading processes and thereafter is highly pseudoplastic; perhaps the superior resistance of this polymer to strike-through is due to this region of high dilatancy at low shear rates.

The superior performance of polymer D in high-speed spreading applications is probably due to the fact that it gives a lower viscosity than the other polymers and has superior viscosity aging characteristics.

A linear regression analysis was carried out on the plasticizer viscosities together with the paste viscosities obtained at age 1 hr and at a shear rate of 11.38 sec^{-1} . The regression coefficient was calculated to be 0.85, which would appear to indicate a fairly high degree of correlation. The standard error of estimate, however, was large, and when the "best" straight line was drawn, it could be seen that there was large scattering about this line. The points were quite evenly distributed about the line, but very few actually lay on it or near it.

The paste viscosity is, therefore, not primarily dependent upon the plasticizer viscosity. The solvating action of the plasticizer on the polymer must have a large effect on the initial paste viscosity as well as on its aging characteristics.

DBP is seen to cause severe paste aging, and presumably this limits the use of this plasticizer in PVC pastes. Other plasticizers which show a marked, but less severe, aging effect are DIBP and BBP.

It is interesting to note how minor changes in the chemical nature of the plasticizer change its effect upon paste viscosity. For example, DAP and Bisoflex L79P are chemically very similar and differ only in that the latter is derived from the essentially linear C_{7-9} alcohols, whereas the former contains more branches and cyclic structures. This difference gives rise to a lower viscosity in the case of the paste based upon Bisoflex L79P. A similar comparison applies in the case of DIBP and Bisoflex L911P.

The amount and nature of the plasticizer used and the age of the paste significantly affect its rheological properties. Several pastes in Table III have a higher apparent viscosity at 1138 sec^{-1} than at 11.28 sec^{-1} , and this is reversed on aging in many cases.

The term "thixotropy" is widely used by PVC paste technologists. This phenomenon is readily detected at low shear rates using the rheogoniometer UV recorder technique described in this paper; thixotropy will cause a drop in the shear stress with time trace given by the recorder, a drop which is recovered by arresting the application of shear. It is interesting to note that none of the pastes described in this paper exhibited thixotropy at low shear rates, and it is suspected by the authors that thixotropy in a PVC paste is rare.

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References

1. J. R. Van Wazer, J. W. Lyons, K. Y. Kim, and R. E. Colwell, *Viscosity and Flow Measurements*, Interscience, New York, 1963.
2. C. Cawthra, G. P. Pearson, and W. R. Moore, *Plastics & Polymers*, April (1965).
3. D. S. Newton and J. A. Cronin, *British Plastics*, October (1958).
4. A. S. Lodge, *Elastic Liquids*, Academic Press, London, 1964.
5. F. R. Eirich, *Rheology, Theory and Application*. Vol. I, Academic Press, New York, 1956.
6. G. W. Scott-Blair, *Elementary Rheology*, Academic Press, London, 1969.
7. T. Gillespie, *J. Colloid Interfac. Sci.*, **22**(6), 554 (1966).
8. P. Sherman, *Industrial Rheology*, Academic Press, London, 1970.

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