Effect of Composition on Flow Properties of Polymeric Sealants

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THE FLOW behavior of viscous polymeric substances when investigated over a range of pressure exhibits non-Newtonian behavior. The literature covers the spectrum of behavior exceedingly well. The materials used in this work exhibited exponential dependence of shear rate on shear stress. The equation which fits the data is

$$F^N = \eta G \tag{1}$$

where

G = shear rate, sec.$^{-1}$
F = shear stress, dynes per sq. cm.
N = exponent indicative of degree to which material is non-Newtonian
η = pseudoviscosity

Such behavior has been reviewed (*1–3*).

As part of a study on the synthesis and evaluation of polymeric sealants, the aim of this work was to show the dependence of quantities similar to N and η on composition in a five-component system.

To enhance the precision of the data and correlations, instrument constants have not been incorporated in the calculations. Pressure and flow rate instead of shear stress and shear rate are reported. Thus, all correlations become sensitive to experimental discrepancies. Such sensitivities are partial tests of derived quantities.

EXPERIMENTAL

The system contained polybutene (Vistanex B-100, Enjay Corp., Division of Standard Oil Co. of New Jersey), microcrystalline wax (Flexo Wax C, Glyco Products Co., Inc.), rosin ester (Staybellite Ester No. 10, Hercules Powder Co.), white petroleum jelly (Vaseline), and Lamp Black Type A (Godfrey L. Cabot, Inc.).

The mixtures were formulated by making a masterbatch of polybutene, microcrystalline wax, and lamp black in a ratio of 15:15:1, on a rubber mill. To this mixture, which had been melted and heated to 150° C., various quantities of the other components were added with stirring. An oil bath was maintained at constant temperature ±1° C. Table I shows the range of compositions investigated. Lamp black concentration was constant throughout. For convenience, the wax and rosin concentrations were grouped as a ratio. Although not apparent from examination of the table, two types of optical sealants were formulated, rotary and static. The former are soft and pliable and the latter relatively stiff and tough.

Flow properties of these formulations were determined with the apparatus shown in Figure 1. The assembled unit was mounted in a Carver press (laboratory type), and the time required to extrude a given volume of material was determined at various pressures. Pressures were maintained constant within 1 or 2%. Extrusion times reproducible within 0.2 second for five to ten readings were assumed to constitute valid data points.

Table I. Weight per Cent Sealant Compositions[a]

Sample No.	Vistanex B-100	Micro-stalline Wax	Rosin Ester	Petroleum Jelly	Ratio, Wax to Resin
1	15	21.9	57.6	24.5	0.58
2	10	23.8	40.7	24.5	0.58
3	5	25.6	32.9	24.5	0.58
4	15	39.9	39.9	4.2	1.0
5	10	42.4	42.4	4.2	1.0
6	5	44.9	44.9	4.2	1.0
7	2.5	26.5	45.5	24.5	0.58
8	2.5	46.6	46.6	4.2	1.0
9	10	27.3	46.7	15	0.58
10	10	25.4	43.6	20	0.58
11	10	21.7	37.3	30	0.58
12	1.0	27.1	46.4	24.5	0.58
13	1.0	46.7	46.7	4.5	1.0
14	10	18.4	46.1	24.5	0.4
15	10	28.7	35.8	24.5	0.8
16	10	32.2	32.2	24.5	1.0
17	10	44.5	44.5	0	1.0
18	10	40.5	40.5	8.0	1.0
19	10	38.5	38.5	12	1.0
20	10	31.7	52.8	4.5	0.6
21	10	37.6	46.9	4.5	0.8
22	10	46.1	38.4	4.5	1.2

[a] Lamp black, constant at 1%.

The entire assembly was made of precision machined brass. The plunger fitted the loading chamber exactly. Several grooves 0.0005 inch deep were machined in it to permit air to escape. When changing from one formulation to another the apparatus was completely disassembled, carefully cleaned with solvent, and dried before refilling.

RESULTS

In Figure 2 are logarithmic plots of flow rate *vs.* pressure. The plots are linear. The equation which fits the data is obviously

$$\ln P = S \ln V + \ln C \tag{2}$$

or

$$P = CV^S \tag{3}$$

P = pressure, p.s.i.g.
S = slope of curves
C = derived constant = P when $V = 1$
V = flow rate, inches per second

Equation 3, although somewhat different in detail from Equation 1, is of the same general form.

$$P^{1/S} = C^{1/S} V \tag{4}$$

S^{-1} is then a measure of the degree to which the material is non-Newtonian and $C^{1/S}$ represents a pseudoviscosity.

Had the pressure and flow rate been transformed to shear stress and shear rate, S would still be the same. Only P, V, and C would be different numerically. The same constant, $R/2L$ (R = radius and L = length of nozzle), multiplies P and C. Because the primary purpose is to show the effect of composition on flow properties in general and on S and C specifically, such a numerical manipulation serves no useful purpose.

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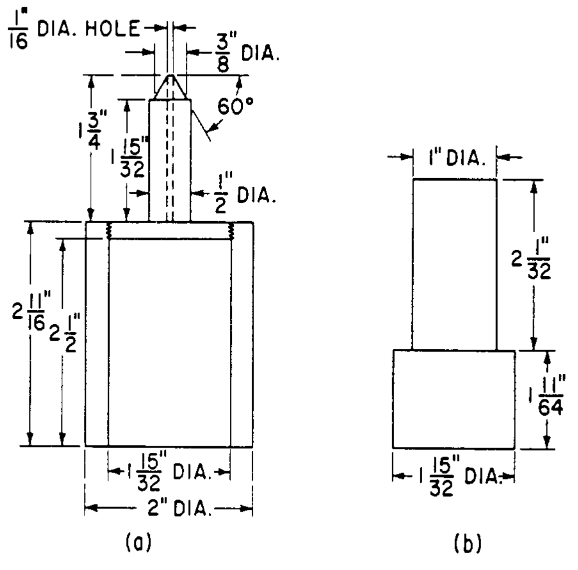

Figure 1. Rheometer

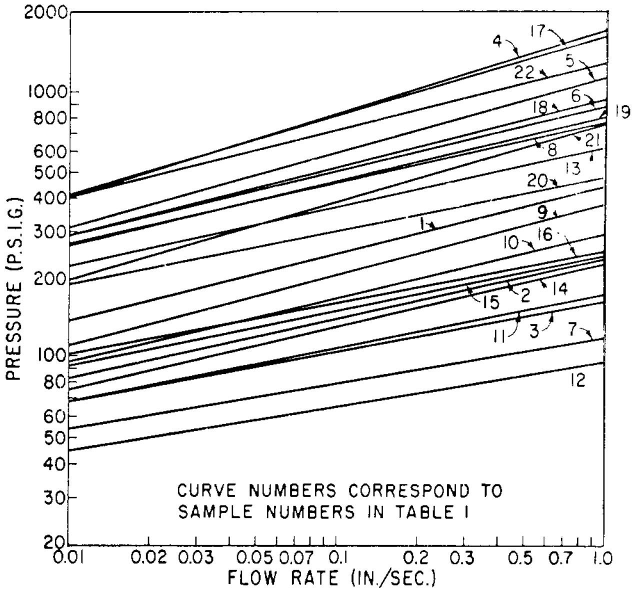

Figure 2. Relation of pressure to flow rate

S as a Function of Composition. The slopes of the curves in Figure 2 vary from one material composition to another. Their dependence on composition was derived by plotting X, Y, Z, V, and W (Table II) on rectangular coordinates as a function of S as shown in Figure 3. The plots are linear. Therefore, $\partial S/\partial X = b_1$, $\partial S/\partial Y = b_2$, $\partial S/\partial Z = b_3$, $\partial S/\partial V = b_4$, and $\partial S/\partial W = b_5$. Table II gives the values of b_1, b_2, etc.

Figure 3 shows that $\partial S/\partial f$ (composition) for rotary and static sealants are identical.

As $W = Z/V$, it is assumed that $S = S'(X,Y,Z,V)$, only

$$S = S_0 + b_1X + b_2Y + b_3Z + b_4V \qquad (5)$$

As $b_3 = -b_4$

$$S = S_0 + b_1X + b_2Y + b_3(Z - V) \qquad (6)$$

The relation of Z to V is known and varies from sealant to sealant. Therefore the equation assumed is

$$S = S_0 + b_1X + b_2Y + b_3(Z - V)W \qquad (7)$$

Multiplying and rearranging give

$$S = S_0 + b_1X + b_2Y + b_3Z(W - 1) \qquad (8)$$

Because all values in Equation 8 are known except S_0, Equation 8 can be tested by determining the numerical value of S_0 over all compositions (Table III).

$$b_1 + b_2 + b_3 + b_4 = 0.230$$

Using $0.230 = S_0$ gives a standard deviation = 0.0055 or 2.4%, since $b_3 + b_4 = 0$

$$S = b_1 + b_2 + b_1X + b_2Y + b_3Z(W - 1) \qquad (9)$$

is the equation which represents the relation of S to composition. Such a small deviation is well within experimental and correlatory errors.

Equation 9 resembles a multiple Taylor series in which higher terms have been eliminated.

Assume $S = S'(X,Y,Z,W)$. Then the multiple Taylor series is

$$S = (S_0) + \left(\frac{\partial S}{\partial X}\right)_0 (X - X_0) + \left(\frac{\partial S}{\partial Y}\right)_0 (Y - Y_0) + \left(\frac{\partial S}{\partial Z}\right)_0 (Z - Z_0) + \left(\frac{\partial S}{\partial W}\right)_0 (W - W_0) + \left(\frac{\partial^2 S}{\partial X^2}\right)_0 (X - X_0)^2 +$$
$$\left(\frac{\partial^2 S}{\partial Y^2}\right)_0 (Y - Y_0)^2 + \left(\frac{\partial^2 S}{\partial Z^2}\right)_0 (Z - Z_0)^2 + \left(\frac{\partial^2 S}{\partial W^2}\right)_0 (W - W_0)^2 +$$
$$\left(\frac{\partial^2 S}{\partial X \partial Y}\right)_0 (X - X_0)(Y - Y_0) + \left(\frac{\partial^2 S}{\partial X \partial Z}\right)_0 (X - X_0)(Z - Z_0) +$$
$$\left(\frac{\partial^2 S}{\partial X \partial W}\right)_0 (X - X_0)(W - W_0) + \left(\frac{\partial^2 S}{\partial Y \partial Z}\right)_0 (Y - Y_0)(Z - Z_0) +$$
$$\left(\frac{\partial^2 S}{\partial Y \partial W}\right)_0 (Y - Y_0)(W - W_0) +$$
$$\left(\frac{\partial^2 S}{\partial Z \partial W}\right)_0 (Z - Z_0)(W - W_0) + \ldots \qquad (11)$$

The relations between S and X, and S and Y are independent; those between S and Z, and S and W are not.

Table II. Code and Slopes of S vs. Composition Plots

Symbol	Component,	b Values
X	Vistanex B-100	$+0.625 = b_1$
Y	Petrolatum	$-0.395 = b_2$
Z	Microcrystalline wax	$-0.331 = b_3$
V	Rosin ester	$+0.331 = b_4$
W	Z/V	$-0.081 = b_5$

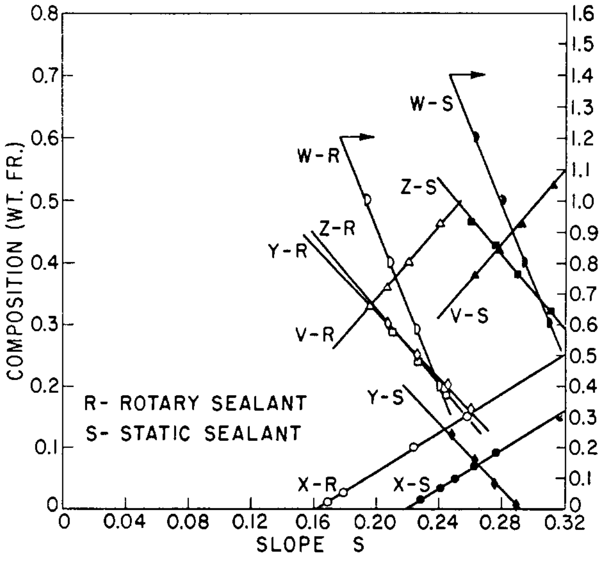

Figure 3. Plot of slope, S, vs. composition

Table III. Check of Equation 8

Sample No.[a]	S_o[b]	Sample No.[a]	S_o[b]	Sample No.[a]	S_o[b]
1	0.229	8	0.236	15	0.223
2	0.227	9	0.222	16	0.231
3	0.224	10	0.224	17	0.232
4	0.235	11	0.231	18	0.233
5	0.234	12	0.221	19	0.223
6	0.236	13	0.236	20	0.222
7	0.222	14	0.232	21	0.224

[a] Average, 0.229. Standard deviation = 0.0053, 2.3%.
[b] Same as sample number in Table I.

Therefore, all second-order terms in the expansion can be dropped except $\left(\frac{\partial^2 S}{\partial Z \partial W}\right)_0 (Z - Z_0)(W - W_0)$.

Rewriting and dropping the appropriate terms in Equation 11

$$S = S_0 + d_1(X - X_0) + d_2(Y - Y_0) + d_3(Z - Z_0) + d_4(W - W_0) + K_1(W - W_0)(Z - Z_0) \quad (12)$$

Let Equation 12 be tested against the empirically derived Equation 8.

When $X = X_0$, $Y = Y_0$, etc., then $S = S_0$. All d values equal slopes of curves of S as a function of the variables evaluated at point zero. K_1 is proportional to the second partial derivative and S is the value of the function at the same point.

Equation 12 may be rewritten

$$S = S_0 + d_1(X - X_0) + d_2(Y - Y_0) + d_3(Z - Z_0) + d_4(W - W_0) + K_1(ZW - Z_0W - ZW_0 + Z_0W_0) \quad (13)$$

let

$$e_1 = S_0 - (d_1X_0 + d_2Y_0 + d_3Z_0 + d_4W_0 - K_1Z_0W_0) \quad (14)$$

then

$$S = e_1 + d_1X + d_2Y + d_3Z + d_4W + K_1ZW - K_1ZW_0 - K_1Z_0W \quad (15)$$

let $e_3 = (d_3 - K_1W_0)$ and $e_4 = (d_4 - K_1Z_0)$, then

$$S = e_1 + d_1X + d_2Y + e_3Z + e_4W + K_1ZW \quad (16)$$

Rearrangement has not altered the equation: When $X = X_0$, $Y = Y_0$, etc.; $S = S_0$. Rearranging the last three terms in Equation 16

$$e_3Z + e_4W + K_1ZW = K_1\left[ZW + \left(\frac{e_3}{K_1}\right)Z + \left(\frac{e_4}{K_1}\right)W\right] \quad (17)$$

or

$$e_3Z + e_4W + K_1ZW = K_1\left[\left(Z + \frac{e_4}{K_1}\right)\left(W + \frac{e_3}{K_1}\right) - \frac{e_3e_4}{K_1^2}\right] \quad (18)$$

substituting Equation 18 into Equation 16 and rearranging;

$$S = e_1 - \frac{e_3e_4}{K_1} + d_1X + d_2Y + K_1(Z + \frac{e_4}{K_1})\ (W + \frac{e_3}{K_1}) \quad (19)$$

Equation 19 is similar to Equation 8, therefore by comparison,

$$e_1 - \frac{e_3e_4}{K_1} = b_1 + b_2;\ d_1 = b_1;\ d_2 = b_2;\ K_1 = b_3;\ \frac{e_4}{K_1} = 0;\ \frac{e_3}{K_1} = -1$$

Therefore, $e_3 = -K_1 = -b_3$, $e_4 = 0$, and $e_1 = b_1 + b_2$. Inserting these values into Equation 19

$$S = S_0 + d_1X + d_2Y + d_3Z(W - 1)$$

since $d_1 = b_2$ and $d_2 = b_2$, then $d_3 = b_3$ and $S_0 = d_1 + d_2$

$$e_1 = b_1 + b_2 = S_0 - (d_1X_0 + d_2Y_0 + d_3Z_0 + d_4W_0 - K_1Z_0W_0) \quad (20)$$

Substituting for d_3 and d_4

$$e_1 = S_0 - [d_1X_0 + d_2Y_0 + (e_3 + K_1W_0)Z_0 + (e_4 + K_1Z_0)W_0 - K_1Z_0W_0] \quad (21)$$

$$e_1 = S_0 - [d_1X_0 + d_2Y_0 + e_3Z_0 + e_4W_0 + K_1Z_0W_0] \quad (22)$$

since $e_4 = 0$, $e_3 = -b_3 = -d_3 = -K_1$

$$e_1 = S_0 - [d_1X_0 + d_2Y_0 + d_3Z_0(W_0 - 1)] \quad (23)$$

Therefore at point zero

$$S_0 = d_1 + d_2 + d_1X_0 + d_2Y_0 + d_3Z_0\ (W_0 - 1) \quad (24)$$

Equation 24 is also identical to Equation 8, when $X - X_0$, $Y = Y_0$, etc.

C as a Function of Composition. The derivation of C as a function of composition is very similar to that for S with two exceptions. C is an exponential function and the slopes (Table IV) of the curves ln C *vs.* composition (Figure 4) are not the same for rotary and static sealants for the same component. The equation derived empirically is

$$\ln C = \ln C_0 + \frac{2.915X}{W} - 2.18Y + 3.01\,(Z - V)(1 - WY) - WY \quad (25)$$

Equation 25 can be checked as before, by computing values of ln C_0 over all compositions (Table V). Therefore Equation 25 depicts the effects of composition on the quantity C well within the limits of experimental and correlatory precision.

Table IV. Slopes of Curves ln C vs. Composition

Component	Slope Rotary sealant	 Static sealant
X	+5.00	+2.915
Y	−2.18	−2.18
Z	+3.01	+0.328
V	−3.01	−0.328

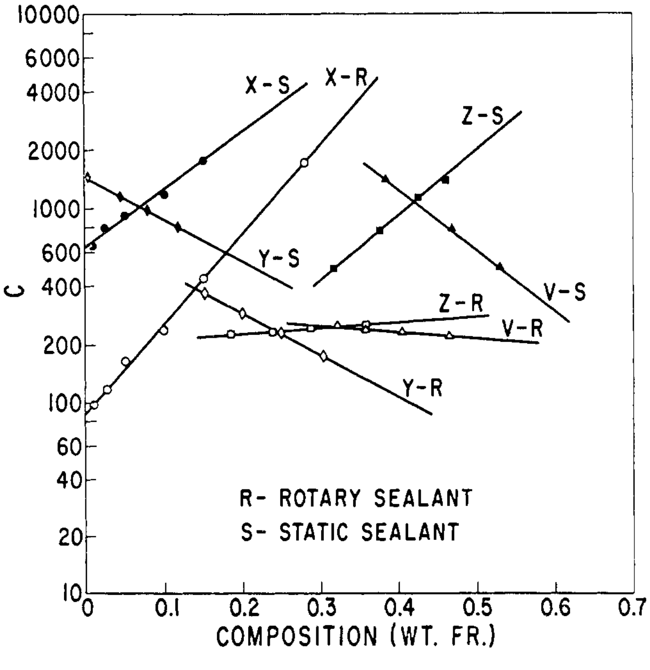

Figure 4. Plot of C vs. weight fraction

Table V. Check of Equation 25

Sample No.[a]	$\ln C_0$[b]	Sample No.[a]	$\ln C_0$[b]	Sample No.[a]	$\ln C_0$[b]
1	2.97	8	2.95	15	2.92
2	2.98	9	3.01	16	2.88
3	3.04	10	3.00	17	2.91
4	2.93	11	2.95	18	2.95
5	2.92	12	3.08	19	2.99
6	2.94	13	2.98	20	2.96
7	3.06	14	3.00	21	2.93
				22	2.87

[a] Same samples as in Table I.

[b] Average $\ln C_0 = 2.96$. Standard deviation = 0.054, 1.8%.

As before, this equation can be derived by a multiple Taylor series. Assume $\ln C = f(X/W, Y, Z, W, V)$. The function is expanded to include third-order terms as shown earlier. Examination of experimental results shows that two third-order terms in ZWY and VWY, all second-order terms in WY, and four first order terms in X/W, Y, Z, and V are preserved. The remainder drop out.

Then by analogy,

$$\ln C = \ln C_0 + a_1 X/W + a_2 Y + a_3 Z + a_4 V + a_5 WY + a_6 ZWY + a_7 VWY \qquad (26)$$

$a_1 = 2.915 \qquad a_3 = -a_4 = -a_6 = a_7 = 3.01$

$a_2 = -2.18 \qquad a_5 = 1$

Both Equations 25 and 8 are more precise if X_0, Y_0, etc., are included. It was shown that

$$-e_3 = (b_3 - K_1 W_0);\ e_3 = -b_3 = -K_1;\ -b_3 = b_3 - b_3 W_0$$

therefore, $W_0 = 2$. Similarly, $Z_0 = 0.248$ and $V_0 = 0.124$. Assume

$$S_0 = b_1 X_0 + b_2 Y_0 + b_3 Z_0 (W_0 - 1) \qquad (27)$$

and let $C' = \ln C$ and $C'_0 = \ln C_0$; then

$$C' = C'_0 + a_1 X/W + a_2 Y + a_3 [(Z - V)(1 - WY)] - WY \qquad (28)$$

Assume

$$-C'_0 = a_1 X_0/W_0 + a_2 Y_0 + a_3 (Z_0 - V_0)\ (1 - W_0 Y_0) - W_0 Y_0 \qquad (29)$$

If there are values of X_0, Y_0, Z_0, V_0, and W_0 that will satisfy Equations 27 and 29, a more exact expression for both may be written. Values of X_0 and Y_0 were plotted for both equations. Straight lines which crossed at a single point resulted. These values of X_0 and Y_0, when substituted into Equations 27 and 29 along with those for Z_0, V_0, and W_0, gave correct results for S_0 and C_0 ($X_0 = 1.13$, $Y_0 = 1.01$). X_0 and Y_0 can also be derived algebracically.

The final equations utilizing the X_0, Y_0, etc., values for C and S are

$$S = b_1 (X - 1.13) + b_2 (Y - 1.01) + b_3 (Z - 0.248)(W - 3) \qquad (30)$$

$$C = \exp \left[-1 + a_1 \frac{X - 1.13}{W - 2} + a_2 (Y - 1.01) + a_3 (1.01 W - WY + 2Y - 1.01)\ (Z - V - 0.124) - (W - 2)\ (Y - 1.01) \right] \qquad (31)$$

The final equation depicting the flow properties can be written

$$1/S \ln P = 1/S \ln C + \ln V \qquad (32)$$

where S and C are given by Equations 30 and 31 respectively. Equation 32 is the logarithmic form of Equation 4.

DISCUSSION

An equation for flow properties as a function of composition for a complex multicomponent mixture can be derived rather easily, the number of experiments necessary to permit such a derivation are relatively few, and the range of possible compositions and fluidities to which the derived equation applies varies over a very large range. The consistencies of the mixtures varied from that of a low viscosity oil to a very heavy axle grease.

In addition to showing the effect of composition of flow properties, the derived equation and the plots of S and C *vs.* composition show the effect of change in composition of each component on the over-all flow properties, the interactions of ingredients if any, and the relative importance of constants S and C.

Figures 3 and 4 demonstrate the effects of changes in concentration of each of the constituents on S and C. Equation 30 shows that microcrystalline wax and rosin ester interact in the expression for S. Equation 31, for C, indicates that none of the ingredients are totally independent. In Equation 32, S is an exponent; therefore, small changes in its numerical value will produce large changes in P, C, and as a consequence in V.

Although flow properties are not of paramount importance in the formulation of printing inks, mastics, sealants, adhesives, etc., they must always be considered. Such products usually contain a multiplicity of ingredients, so that physical and chemical properties suited to the application result. Because there is no way at present to predict their flow properties, the manufacturer usually takes what he gets or modifies his formulation, using trial and error techniques, to yield the flow characteristics required for the application. Such a procedure is tedious, random, time-consuming, and expensive. If the derivation shown here is applicable to systems other than the one studied, then a method for characterizing the flow properties as a function of the nature and concentration of a basic set of ingredients is available. As shown, the number of experiments is small, the apparatus, required simple, and interpretation of the data and derivation of the suitable equations rather elementary. Because, the chemical components were not unusual and the range of concentrations did not appear to impair the validity of the correlations, it seems likely that these techniques will be applicable to other similar systems. Certainly, the possible savings in time and labor alone make the investigation of this possibility worthwhile.

ACKNOWLEDGMENT

The authors are indebted to Selby M. Skinner, Chemistry and Chemical Engineering Department, Case Institute of Technology, for many helpful discussions and suggestions, and to the Ordnance Department, Franklin Arsenal, Philadelphia, Pa., which supported the work.

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RECEIVED for review May 20, 1959. Accepted November 9, 1959.