ON THE DIELECTRIC ABSORPTION PHENOMENA IN PLASTICIZED POLYVINYL CHLORIDE BY POLARITY REVERSAL METHOD OF DIRECT CURRENT VOLTAGE

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1. Introduction

When direct current voltage is applied to liquid or solid dielectrics a transient current as a function of time is observed. This phenomenon is well-known as dielectric absorption. Hitherto, a number of investigations have been made on this phenomenon, in which the space charge accumulation or the electric dipole orientation plays an important role as reported by Jaffé[1] and Munick[2] etc.

In the present investigation measurements were made of the transient current-time (*I-t*) characteristics following to the polarity reversal of the applied voltage on the plasticized polyvinyl chloride, in which the ion mobility is able to control widely due to the variation of plasticizer concentration and temperature. Throughout our experiment, the peculiar phenomena on the *I-t* characteristics which are not understood with the factors mentioned above were observed in the region of the relatively high current density. This paper gives the results of investigating such peculiar phenomena from the standpoints of applied voltage, plasticizer concentration and temperature etc. and discussing their mechanisms experimentally and theoretically.

2. Experimental Procedure

Samples are moulded in a sheet form, about 10 cm in square and 0.5 mm thick, and are mixed with 0–100 parts of plasticizer, dibutylphthalate (DBP) and a small amount of stabilizer for 100 parts of polyvinyl chlcride (PVC). The silver conducting paint is adopted to form the parallel plane circular electrodes, 6 cm in diameter, with the guard-ring.

The applied voltage is supplied from the stabilized 1,000 volt d.c. source and the change of voltage is made by the resistance divider. The blook diagram of the experimental circuit is indicated shematically in Fig. 1. The samples are kept in a thermostatic oven to investigate the temperature dependence of *I-t* characteristics between room temperature and about 90° C, which are measured by the thermo-couple element inserted between the guard-ring and the test sample. The operation of polarity reversal of applied voltage finishes within a short time as possible by the switch K_1 in Fig. 1.
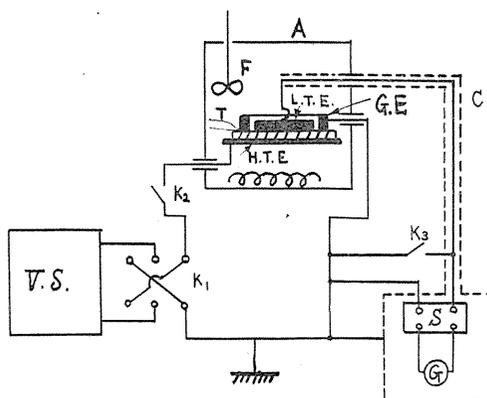
FIG. 1. Block diagram of experimental circuit.

V.S.: Stabilized 1000 volt d.c. source, H.T.E. and L.T.E.: Electrode at high and low voltage side respectively, G.E.: Guarded elctrode, S: Current shunt, G: Galvanometer, T: Thermocouple element, A: Thermostatic oven, C: Shielding, K_1, K_2, K_3: Switchs, F: Fun.

3. Experimental Results

### 3-1. I-t characteristics in the testing of polarity reversal of applied voltage

Fig. 2 (A) and (B) represent two typical tendencies of I-t characteristics after the voltage application to the undisturbed specimens at $t=0$, which includes sudden reversal of voltage polarity at certain time successively. Fig. 2 (A) indicates the result on the sample consisting only of PVC in whch the current is relatively small since the density of impurity ions is not small, but the ion mobility is extremely small. As shown in the curve (1), when 1,000 volt is applied to the sample undisturibed at $t=0$, the current decreases rapidly from large value of it after the geometric capacitive current diminishes and arrives at the equilibrium value I_∞ which corresponds to the leakage current or the conduction current, within about 10 min. If the voltage polarity is reversed instantaniously at this equilibrium state as shown in the figure, the reversal of the current direction takes place and successively the absolute value of the current decreases with time from large value to small one. This process given by the curve (2) is almost the same with that of the curve (1). The absorption phenomena reported on most liquid or solid dielectrics represent these tendencies without fail[2][3].

On the other hand, Fig. 2 (B) represents the result on the sample composed of 100 parts PVC and 85 parts DBP, in which the mixture of plasticizer increases the ion mobility considerably, consequently the current is relatively large. Here the first voltage application to the undisturbed sample at $t=0$, brings about the current change with time similar to that of the curve (1) in Fig. 2 (A). As shown with the curve (2) in Fig. 2 (B), however, the I-t characteristics after reversing the voltage polarity at the time when dI/dt becomes negligible is completely different from that of the curve (2) in Fig. 2 (A); due to the polarity reversal of the voltage, the current direction changes oppositely and the absolute value of the current just after reversal keeps the same as just before and increases
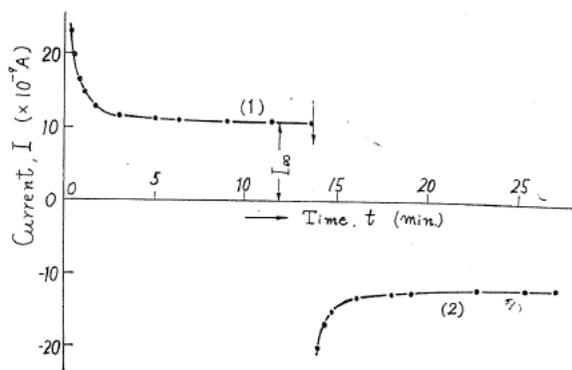
(A)

Sample: PVC(100)-DBP(0), V=1,000 volt, T=80°C
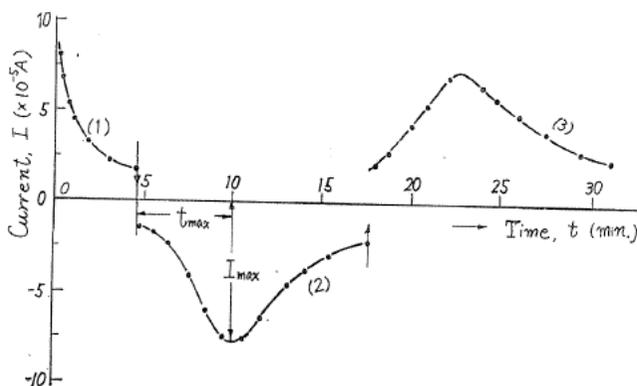
(B)

Sample: PVC(100)-DBP(85), V=1,000 volt, T=30°C

FIG. 2. Two different types of I-t characteristics after reversal of voltage polarity, (A) shows normal I-t curve and (B) gives peculiar I-t curve. Voltage polarity is reversed at the time referred with the mark ↓.

with time to the maximum value (I_{max}) and after that decreases toward a constant value. And again reversing the voltage polarity at the point of the constant current, the current as shown in Fig. 2 (B) the curve (3) follows nearly the same trace as the curve (2).

The papers referring to these phenomena have hardly been seen in the past. In the report by Mead and Fouss[3], investigating on the conduction phenomena of PVC resin with the organic electrolytes as an impurity using the similar procedure as mentioned above, while they pointed out that conductivity σ gives a maximum value at certain time on σ-t curve though it is not so evident as our results mentioned above with I-t curve, they did not refer in detail to the cause of these phenomena. Then we investigated on the influences of temperature, plasticizer concentration and voltage etc, to these phenomena so as to identify on what kind of mechanism these peculiar phenomena depend. It is to be noted

that these phenomena depend on the parameters mentioned above rather regularly as indicated in the following sections.

3-2. Influence of plasticizer concentration to I-t characteristics

The changing characteristics of these phenomena with various plasticizer concentrations are shown in Fig. 3, which illustlate only the situation after the polarity reversal of applied voltage.

In Fig. 3, the increasing rate of current to time dI/dt and I_{max} increase with quantity of plasticizer in parts for 100 parts PVC (hereafter referred to as $\overline{PL}$) and t_{max} decreases rapidly with $\overline{PL}$, where I_{max} and t_{max} are defined in Fig. 2 (B). The values of I_{max} and t_{max} on the samples with various $\overline{PL}$ are collected in Table 1. According to the fact that the mixture of plasticizer brings the decrease of the internal viscosity of the sample which is connected with the ion mobility in the relation of inverse proportion approximately[4], it may be suggested that the forms of $I-t$ characteristics depend in part on the change of ion mobility.
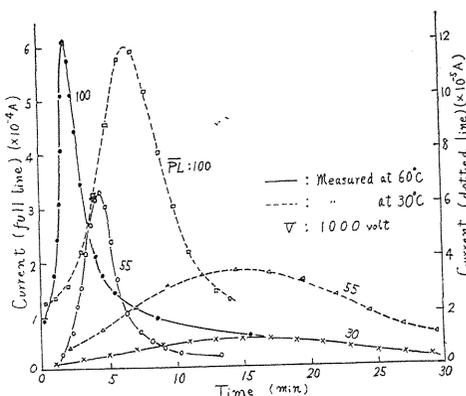

FIG. 3. Variation of $I-t$ characteristics on various samples with different quantities of plasticizer, $\overline{PL}$ in parts for 100 parts of PVC indicated by the number on each curve.

TABLE 1. I_{max} and t_{max} as a function of $\overline{PL}$

		Plasticizer quantity, $\overline{PL}$ (parts)			
		30	55	85	100
Temp. 30°C	I_{max} (A) t_{max} (min.)	— —	3.6×10^{-5} 14.5	7.8×10^{-5} 6.5	12×10^{-5} 6.4
Temp. 60°C	I_{max} (A) t_{max} (min.)	5.3×10^{-5} 15	3.35×10^{-4} 4.4	— —	6×10^{-4} 2

V: 1,000 volt.

3-3. Temperature dependence of I-t characteristics

The change of ion mobility in plasticized PVC also occurs when the temperature is varied, bacause the temperature dependence on the viscosity η can be discribed in the following equation,

$$\eta = K \exp (U/kT) \tag{1}$$

where U is activation energy for viscous flow, k Boltzman constant, T absolute temp. and K constant. Hence it is expected that the temperature dependence of $I-t$ characteristics has similarity to the former case changed with the quantity of $\overline{PL}$, if these characteristics are to be related to the change of ion mobility. Fig.

4 is an example of temperatere dependence of I-t characteristics, which proves the above assumption. The peak points of the curves remove to the left side as temperature increases. In Fig. 5, such t_{max} is given as a function of temperature on various samples with different $\overline{PL}$.

Next, the property of I_{max} referred in Fig. 2 is analyzed more in detail, which is one of the important factors specializing these phenomena. Fig. 6 indicates the logarithmic plots of I_{max}, given by the full line in the figure, as a function of $10^3/T(^\circ K)$ and the relation between I_{max} and T is represented by the following equation;

$$I_{max} = A \exp \left(-E_{I_{max}}/RT \right) \tag{2}$$

where A is constant. This relation is equivalent to that of ionic conduction[4], therefore $E_{I_{max}}$ gives the activation energy for I_{max} if R represents gas constant. Such $E_{I_{max}}$ relating to different $\overline{PL}$ are collected in Table 2, which decrease with $\overline{PL}$. The changes of the equilibrium leakage current I_∞, referred in Fig. 2, are also drawn in Fig. 6 and they show the equal tendencies to the equation (2) approximately except the line for $\overline{PL}$: 30 parts. E_{I_∞}, activation energy for I_∞, has
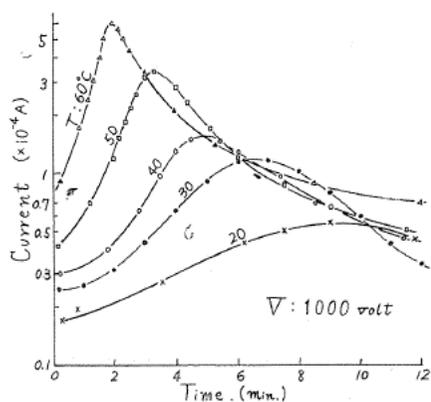

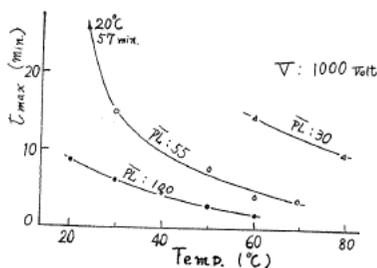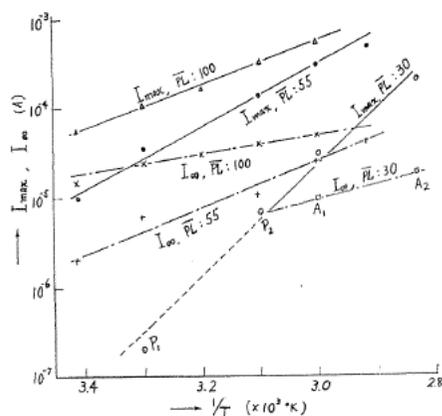FIG. 4. Temperature dependence of I-t characteristics of a sample with $\overline{PL}$: 100.

FIG. 6. Temperature dependence of I_{max} and I_∞, shown in Fig. 2, as a function of $1/T$ on various samples with different $\overline{PL}$.

FIG. 5. The t_{max} as a function of temperature on samples with different $\overline{PL}$.

TABLE 2. Activation energy for I_{max} and I_∞

Activation energy (kcal/mol)	Plasticizer quantity, $\overline{PL}$ (parts)			
	30	55	85	100
$E_{I_{max}}$	27.7	17.6	12.7	11.4
E_{I_∞}	—	12.8	7.6	4.9

fairly smaller value than $E_{I_{max}}$ and there is defference by about 5 kcal/mol as indicated in Table 2. What should be noted here in the case of $\overline{PL}$: 30 parts about Fig. 6 is that the I_{max} values observed at rather higher temperature than 50°C exist on the linearly extended line which connects P1 and P2 representing the equilibrium leakage currents I_∞ at 30°C and 50°C respectively where the I-t characteristics exhibit the usual absorption phenomena characterised in Fig. 2 (A), while A1 and A2 representing I_∞ at rather higher temperature are far below this line. Therefore it is difficult to regard P1 and P2 as belonging to A1 and A2 group. According to the above facts, it may be suggested that in the peculiar I-t characteristics, I_∞ given by A1 and A2 possess different factors from those of the usual equilibrium leakage currents like P1 and P2 and I_{max} has important significance for the estimation of true leakage current in the peculiar I-t characteristics. Combing the above results with those of the previous section it becomes clear that these peculiar phenomena are closely connected with ion mobility.

3-4. Influence of applied voltage on I-t characteristics

Fig. 7 indicates the voltage dependence of I-t characteristics after the voltage polarity reversal. The variations of the applied voltage provide the peculiar phenomena with wide changes of I_{max} and t_{max}, which are regular relatively and are similar to those caused by $\overline{PL}$ quantity and temperature. The relations of I_{max} and t_{max} to applied voltage are drawn in Fig. 8 and I_{max} satisfies the following equation, which is equivalent to Ohm's law, under the voltage range tested,
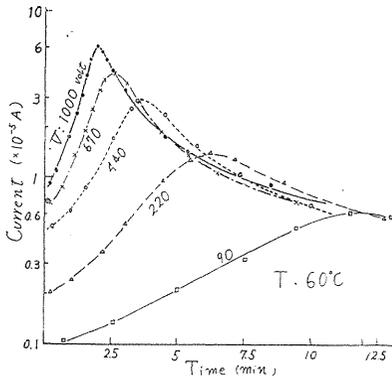
$$I_{max} = kV \tag{3}$$

FIG. 7. Voltage dependence of I-t characteristics on a sample with $\overline{PL}$: 100.
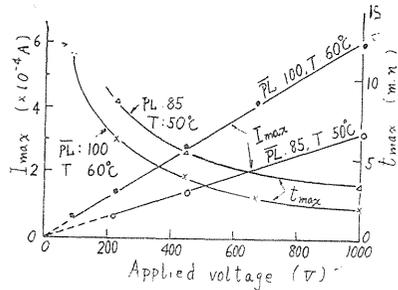
FIG. 8. I_{max} and t_{max} as a function of applied voltage on samples with different $\overline{PL}$ and at various temperatures.

where k is a proportional constant and V is applied voltage. The above mentioned results concerning with the voltage are important, because the variation of voltage within such range does not contribute to the change in ion mobility, but to ion velosity v through the relation, $v = \mu E$, μ being ion mobility and E electric field intensity.

As a result, it can be expected from various experimental facts mentioned above that these peculiar phenomena are closely related to the total electric charges passed across the dielectrics.

4. Discussion

Various mechanisms on the absorption phenomena of solid dielectrics are suggested and among them two main mechanisms are generally admitted; one is of the orientation of electric dipole and another is of the counter e.m.f. caused by the space charge accumulation due to removal of ions. Our test samples, plasticized PVC resins, possess the electric dipoles, which orientate themselves with time after voltage application and contribute to the absorption current I_α as given by the equation (4),

$$I_\alpha = KV\alpha(t) \tag{4)[5]}$$

where K is constant and $\alpha(t)$ is a function representing the temporal decrease, which depends on the distribution of time constant of dipole polarization and is indicated as At^{-n} (A, constant) in the most cases; $n=0.5-1.0$ for the plastic insulators[2]. Generally, the dielectrics containing permanent dipoles show the reversible absorption phenomena and satisfy the principle of superposition for the voltage application[2,5]. Accordingly, our procedure of voltage application as shown in Fig. 9 (A) is equivalent to that of Fig. 9 (B). Thus the current I_α after the time T when the voltage polarity is reversed is able to be written in the equation (5),

$$I_\alpha = KA\{ V(t_1 + T)^{-n} + (- 2 V)t_1^{-n}\} \tag{5}$$

where t_1 is measured from T. I_α given by this equation decreases monotonously, if $t_1>0$, so it is impossible to explain the I-t characteristics including the current increase with time at the initial stage. That is to say, the absorption current caused by the dipole orientation is not a main factor controling these peculiar phenomena.
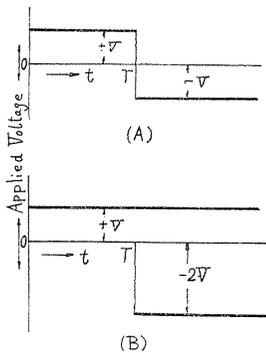

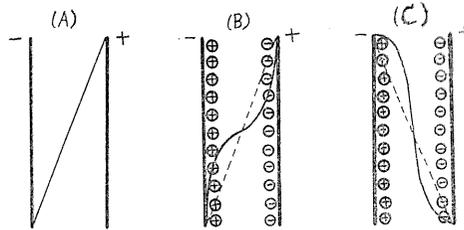FIG. 9. The principle of super-position; Voltage applied in (A) is equivalent to that shown in (B).

FIG. 10. Schematic illustration of potential distribution distorted by space chage formation; the potential distribution at $t=0$ given in (A) is distorted as shown in (B) with passing the time for space charge accumulation near electrodes. (C) indicates the situation just after voltage polarity is reversed, at this instance the space chage distribution be kept in that of (B) state.

Next, discussions are given about the relation between the I-t characteristics observed and the change of internal effective electric field due to the counter e.m.f. based on the space charge formation pointed out by Joffé[1]. Supposing that the removable ions are composed of plus and minus and that the voltage is

applied to the undisturbed sample at $t=0$, the internal electric field, which is almost uniform at $t=0$ like Fig. 10 (A) decreases gradually in the middle part of the sample except near the electrodes as shown in Fig. 10 (B) and then the current reduces its value with time. The reversal of voltage polarity at this situation gives rise to the potential distribution of Fig. 10 (C). As the space charges work additively for a while to the internal electric field just after the reversal, the current followed by decrease from its large value with time may be produed. This current explains the characteristics of Fig. 2 (A), but is hardly consistent with that of Fig. 2 (B).

From various experimental results and discussions mentioned up to here, the variation of movable ion density in the dielectrics caused by current passing may be considered as an important factor to explain the current change with time in these peculiar phenomena. When d.c. voltage is applied to dielectrics and produces ionic current, ions are dissipated at electrodes according to Faraday's electrolysis law[6]. It is indicated by Nakanima[7] about various insulating oils and by Standhammer[8] for cyclohexane that ion density in dielectrics is changed by the ionic condution. Generally, the ion density in dielectrics is determined by three factors; dissociation ion, recombination ion and dissipated ion at electrodes. The movable ions of plasticized PVC as reported in our previous paper[4], are supplied chiefly from the impurities in PVC and the reaction products like HCl caused by the thermal decomposition of PVC. Supposing the rate of creation of ion due to the dissociation is smaller than that of dissipation of ion due to the clean up action of current and the recombination, the movable ions in dielectrics decrease and the current diminishes subsequently. If the voltage polarity is reversed in this situation, it is expected that just after the reversal the ion density is maintained and then the current gives the opposite direction, but the same value with that just before the reversal and the ions collected near electrodes or deposited at electrodes diffuse toward the opposite electrode. Then it may be considered that the current increases till t_{max} when the ion density determined from three factors mentioned above arrives at a maximum value and succesively decreases, because ions gather at the opposite electrode again. Since this process is related to ion velosity, the larger ion mobility and applied voltage the shorter the t_{max} can be provided.

Here the quantitative analysis, especially on the current increasing process is not yet satisfactory, so we are studying on it in more details. We can understand qualitatively, however, these peculiar I-t characteristics with this way of appreciating the experimental results.

As mentioned above, if the ion density in dielectrics is decreased by cleaning up of ions based on ionic current, the substraction of I_∞ out of total current I in the current decreasing process is the current corresponding to the change of ion density. Supposing, as a first approximation, the mono-charged and a kind of ions, the substructed current density $i=(I-I_\infty)/S$ (electrode area) is given by the equation (6),

$$i=eN\mu E \qquad (6)$$

where e is electron charge, N ion density, μ ion mobility and E electric field intensity. On the other hand, the number of ions per unit area, n, dissipated at electrode during the period of 0-t is indicated by the equation (7),

$$n = \int_0^t i\,dt/e. \tag{7}$$

Postulating that the ion density decreases uniformly between electrodes having the spacing d_0 and the change of ion density caused by the dissociation and the recombination is neglegible compared with that of n, the ion density N at the time t is represented as $N_0 - n/d_0$, where N_0 is the ion density at $t=0$. As the result, the i at any moment is indicated as follows;

$$i = eN\mu E = e\mu E\left(N_0 - \int_0^t i\,dt/d_0 e\right) \tag{8}$$

thus, $$i = i_0 \exp\left(-\mu Et/d_0\right) \tag{9}$$

where i_0 is the current density at $t=0$.

Fig. 11 shows the logarithm of the currents, $(i \times S)$ and I as a function of time t, according to the equation (9) on the sample with $\overline{PL}$: 85 parts at 20° C. The substruction $(i \times S)$ of I_∞ from I satisfy the eq. (9) relatively well in the region where the current decreases with time. It is to be noted that the slope of straight line given in Fig. 11 corresponds to the value of $\mu E/d_0$ providing a measure of ion mobility μ. As an example, an estimation of ion mobility according to the above consideration produce a value of 2×10^{-8} cm²/v. sec. under the condition of Fig. 11, that is $d_0 = 0.05$ cm and $E = 2 \times 10^4$v/cm. Furthermore, putting the obtained mobility into the eq. (6) to calculate the ion density for I_{max}, we gain about 3×10^{16} ions/cm³. On these estimations the further investigations and discussions are necessary, because there are many assumptions to obtain the quantitative relation.
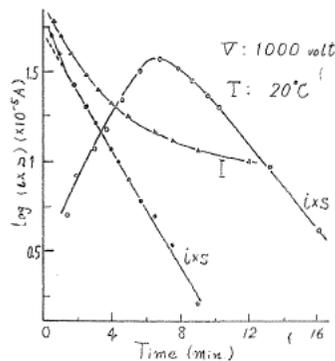

FIG. 11. The logarithm of $i \times S (=I\text{-}I_\infty)$ as a function of t on a sample with $\overline{PL}$; 85, according to the eq. (8).

5. Conclusion

In this paper, using the procedure of voltage polarity reversal the experimental reults are described of the dielectric absorption phenomena of plasticized polyvinylchloride, in which such peculiar current-time characteristics is found by us. From the reslts of plasticizer concentration to be mixed, temperature and applied voltage dependencies on these peculiar I-t characteristics, it is concluded that these phenomena are difficult to be understood by such space charge effect of ion or orientation effect of electric dipole as reported in the past and are closely connected with the variation of internal effective ion density caused by the clean up action based on the ionic conduction current. According to this conclusion, the theoretical equation of I-t characteristics is constructed especially in the region of the current decreasing with time, which is in agreement with the experimental results. Based on the theoretical equation and experimental results, an estimation of ion mobility and ion density for I_{max} referred in Fig. 2 (B) introduces the value

of 2×10^{-8} cm²/v. sec and of about 3×10^{16} ions/cm³ respectively on the sample of PVC 100 parts: DBP (plasticizer) 85 parts, at 20°C.

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