

had fatty feeling and when warm it became sticky. Its nitroso derivative was easily formed. The melting point above mentioned is not quite exact, for this compound did not show sharp melting point. No reaction occurred between 3-nitro carbazole and vinyl ether. Therefore, it is suggested that the reaction product might have been formed by the addition of vinyl ether to the 3rd position of carbazole. Furthermore, when this product was kept in contact with catalyst for a long time three kinds of other products were obtained, molecular weights of which were observed to be 500-600.

b. Reaction of Vinyl Acetate with carbazol.

The reaction was carried out in a similar way to that of vinyl ether. In this case mixture of  $\text{BF}_3$ -etherate and mercuric sulfate was effective. In progress of the reaction, acetic acid splitted out. When benzene was used as solvent, an amorphous solid was obtained. Its molecular weight was observed to be about 400. And it also formed its nitroso derivative. Further details are not known about this reaction product so far.

### 23. The Relation between the Plastic Viscosity and Yield-point of High Polymeric Material.

*Kotaro Tomihisa and Junji Furukawa.*

High polymeric material behaves like an elastic body according to Hook's law (1) within a certain stress limit, the so-called yield-point ( $f$ ), beyond which it flows like a pure viscous liquid showing Bingham's flow (2). Mathematically it is expressed as follows,

$$\tau = \gamma E \quad \text{for } \tau < f \quad (1)$$

$$D = \frac{d\gamma}{dt} = \frac{1}{\eta} (\tau - f) \quad \text{for } \tau > f \quad (2)$$

Where,  $\tau$  is the stress:  $\gamma$ ,  $E$ , and  $\eta$  are the strain, Young's modulus and plastic viscosity of the material respectively.

We used the Goodrich's plastometer for the measurement and calculated  $\eta$  and  $f$  of differently masticated rubbers (i.e. of different polymerities) at various temperatures by means of Scott's formula. [cf. R. Houwink: *Physikalische Eigenschaften u. Feinbau von Natur u. Kunstharz* (Leipzig 1934)].

When these values obtained are plotted on the  $\ln \eta - \ln f$  diagram, they form a linear curve.

From this we conclude that  $f$  shows the same value corresponding to  $\eta$ , if  $\eta$  shows equal values, quite independent of the values of polymerity and that the higher the viscosity, the greater the yield point. As a consequence, when discussing the problem of plastic flow and liquid flow, we need only consider the flow mechanism itself.

Kanamaru measured the fluidities and yield-points of polyvinylbutyral which was plasticized with dibutyl phthalate. When  $\ln \eta$  are plotted against  $\ln f$ , however, they form a line which has a different slope from ours. The reason for this difference may be due to the different ranges of viscosity for the two cases, that is, for the rubber  $10^6$ - $10^{11}$  poises and for the latter  $10^{10}$ - $10^{13}$  poises. We are going to investigate the relation by either elevating or lowering the viscosity by the addition of fillers and plasticizers respectively.

## 24. Theoretical Considerations on the Elasticity of Plasticized Polyvinyl Chloride (PVC).

*Junji Furukawa.*

The author regards the elasticity  $G$  of plasticized PVC as the visco-elasticity. Kuhn gives a formula for the viscoelasticity of polymer, which consists of  $k$  units as follows,

$$G = G_1 e^{-t/\lambda_1} + G_2 e^{-t/\lambda_2} + \dots + G_k e^{-t/\lambda_k}$$

where  $G_1, \dots, G_k$ ,  $\lambda_1, \dots, \lambda_k$  are elasticities and relaxation times of units respectively and  $t$  is time of observation. The author proposes thereof a simplified average formula as follows.

$$G = G_L e^{-t/\bar{\lambda}}$$

$\bar{\lambda}$  is an average relaxation time and is indicated as follows.

$$\bar{\lambda} = \bar{A} e^{\bar{E}/RT}$$

where  $\bar{E}$  and  $\bar{A}$  are the average value of activation energy and entropy of segments respectively. From this formula, the following empirical formula after Dienes will be derived.

$$\frac{\ln G_L - \ln G_H}{\ln G - \ln G_H} = \left( \frac{R}{E} \right)^n T^n = BT^n$$

where  $G_L$  and  $G_H$  are the elasticity at the temperature low and high respectively, while  $B$  and  $n$  are both constants.

Plasticizer added to the polymer lowers the viscosity and the elasticity of the system. Plasticizer of smaller  $\lambda$  shows the higher softening effect and gives greater temperature coefficient of elasticity.

According to the author's theory the plasticizer of smaller  $E/\lambda$  and also smaller  $\lambda$  shows the superior plasticity.

Thus, from the conclusion in consideration of the weight average of  $\lambda$  between plasticizer (1) and polymer (2), was obtained the following equation which indicates that  $\log G$  decreases linearly in accordance with plasticizer content  $W_1$ .

$$\ln G \approx \ln G_L [\ln \lambda_2 - W_1 (\ln \lambda_2 - \ln \lambda_1)] + C$$

Finally, provided that the equation,  $\ln \lambda = A \ln M + B$ , is given, where  $M$  is molecular weight of polymer and  $A, B$  are constants, the following linear relation between  $\ln G$  and  $M$  is obtained.

$$\ln G \approx \ln G_L [A \ln M - \ln t] + C$$