Determination of the Process-Volatility of Plasticizers

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INTRODUCTION

Testing vinyl for real-life performance involves not only the end-product properties of the formulation but its processing characteristics as well. The latter is important since it has a considerable influence on the overall economics of the product.

Volatile loss of some of the vinyl formulation components is an important consideration, particularly in processes such as spread coating. During fusion, the product is exposed to large volumes of fast moving hot air (180-200°C or 360-400°F) required to heat up the vinyl layer. These conditions promote considerable evaporation of the volatile components, especially plasticizer.

Testing plasticizers and plastisols in conventional laboratory ovens may lead to a correct ranking as to process volatility but it usually does not give adequate information regarding the magnitude of the evaporation losses in industrial operations.

In order to simulate plastisol fusion practice, we believe the laboratory method should use conditions similar to those applied in the actual industrial oven. Thus, high air velocity (forced convection) and high air temperature should be applied. In the following paragraphs the required conditions will be more precisely defined and a laboratory procedure to determine the "process-volatility" of plasticizers will be described. Finally, some results obtained with this procedure will be discussed.

PLASTISOL FUSION CONDITIONS IN INDUSTRIAL HOT-AIR OVENS

The following data indicate the range of relevant conditions that are found in industrial practice. The ovens are relatively long, exposing a large surface of vinyl to the circulating hot air. The air temperature typically is 180-200°C (360-400°F). The residence time of the vinyl in the oven ranges from about 20 s to a few minutes, depending on several factors, including coating thickness (typically 0.1-1 mm, 4-40 mils). The relatively short residence time indicates that the heat transfer rate is high, since in less than this short period the vinyl layer must be heated up from room temperature to a level of 170°C (340°F) or higher. This is achieved via a high air velocity, which also promotes evaporation. The air is purged at a rate of 10,000-50,000 m³/h (350,000-1,500,000 SCF/h), thus removing volatilized material. The purge rate is dictated by the requirement to prevent drip at "cold spots" in the oven. On the average, however, the circulating air is far from being saturated. The plasticizer concentration in the purged air is typically of th order of 1 g/m³ (0.03 g/SCF), with considerable variation from case to case, depending on the conditions. It thus follows that plasticizer losses ranging from 10-50 kg/h (20-100 lb/h) may occur. *Table 1* is derived from a paper by H. Delorme (1), supporting the above data.

An analysis of the heat-up of the vinyl layer on its course through the oven has been made using, classical theory as described in the literature (2). In the heat-up process two major steps can be defined. Firstly, the heat transfer rate from the bulk of the air to the vinyl surface plays a role of importance. Secondly, the transfer of heat from the vinyl surface through the inside of the layer may be determining. It can be shown that with a relatively thin vinyl coating and air-heating, the air-to-vinyl heat transfer rate is the main rate-determining step. Thus, th vinyl layer has an approximately uniform temperature across its thickness. This greatly simplifies the mathematical approach. With sufficient precision for the present purposes, the heat-up of the vinyl layer in the oven can thus be described as:

$$\Delta T/\Delta T_o = e^{-kt/ecR} \qquad (1)$$

The meaning of the symbols, together with some typical values for the parameters are shown in *Table 2*. (*Equation 1* should be used applying consistent units, as shown below. For example the

Table 1. Plasticizer Losses in Fusion Ovens

Application	Air purge m³/h	Air purge (SCF/h)	Plasticizer conc. in purge g/m³	Plasticizer conc. in purge (g/SCF)	Calculated loss kg/h	Calculated loss (lb/h)
Coated fabric	12.000	(420,000)	3.0	(0.085)	36	(80)
Cushioned flooring	60.000	(2,100,000)	0.78	(0.022)	47	(100)
Bottle caps	30,000	(1,050,000)	0.28	(0.008)	8.4	(18)

Table 2.

Symbol	Meaning	Typical value
ΔT	Temp. difference hot air—vinyl at time t.	Variable
ΔT_o	Initial temp. difference	160°C (290°F)
t	Time (seconds) elapsed after entrance into the oven.	Variable
k	Heat transfer coefficient air-to-vinyl (depends on degree of air convection)	20-80 J/(m²) (s) (°C) or 4-15 BTU/(ft²) (h) (°F)
s	Density	1200 kg/m³ or 75 lb/ft³
c	Specific heat, vinyl	1800 J/(kg) (°C) or 0.42 BTU/(lb) (°F)
R	Thickness (or half-thickness for two-sided heating) of the vinyl layer.	$0.1 - 1 \times 10^{-3}$ m (4-40 mils)

coating thickness R given in mils, should be recalculated in feet.)

The heat transfer coefficient k is mainly determined by the degree of air convection. The typical value range as shown above reflects the variation in forced air convection that occur in practice, from oven to oven.

Equation 1 closely describes the heat-up of the vinyl layer in the course of time. Substituting the indicated typical values for the parameters (taking $k = 40$ and $R = 0.3$ mm) and calculating the point in time where the vinyl still is 8°C (14.4°F) less than the hot-air temperature (thus, $\Delta T/\Delta T_o = 0.05$) we find: $t = 50$ s. This value is reasonable in the sense that it falls within the range of industrial practice.

The above excursion into theory is useful since it yields quantitative criteria to define a laboratory procedure approaching industrial practice. Any laboratory procedure intended to investigate phenomena associated with industrial fusion operations—such as the process evaporation losses—should use similar forced air convection conditions as those described above. In hot-air ovens the heat transfer rate as well as the evaporation rate of the plasticizer in the plastisol may be expected to be directly related to the degree of air convection.

PROCESS-VOLATILITY: LABORATORY EQUIPMENT AND PROCEDURE

Description

The equipment used in this study is essentially a knife-over-roll spread-coating frame and a precision air-heated oven. The geometry of the oven is similar to that of industrial scale ovens. With the spread-coating unit a coating is applied on a 30 × 30 cm (1 × 1 ft) substrate (release paper, fabric, etc.) held in the frame. The frame with coated substrate slides into the oven under pushbutton control and returns automatically after a preset exposure time that can be varied at will. Air temperatures can be controlled over a wide range. The air circulation rate in the oven is high and can be varied between 500 and 1400 m³/h (17,500-50,000 SCF/h). The sample is heated by the hot-air stream from the top and bottom of the oven. The assembly used is commercially available (Werner-Mathis AG, Zürich/Switzerland; type LTSV/LTF). Any other equipment simulating real-life coating processes may be used, of course.

The experimental procedure is simple. A known amount of plastisol is coated on the substrate. The coated weight can be found by weighing the plasticizer container and the tools used before and after coating. Alternatively, the plastisol can be coated on paper and lightly pregelled. After removing the pregelled sheet from the release paper, a sample can be cut and weighed. The sample can then be placed back on the release paper to be exposed to the desired conditions. After cooling, the exposed sample is removed from the paper and weighed again. The observed weight difference is equal to the amount of plasticizer—and other volatile material, if present—that evaporated during fusion.

Discussion

The procedure has been successfully applied to investigate the difference in process volatility between various plasticizers, including DOP, DINP and DIDP. The loss rates as found with the procedure appear to be comparable to those experienced in industrial practice. The results have been reported (3) and a summary of the results will be discussed further below. In addition it will now be shown that the equipment also closely simulates typical industrial heat-up conditions. *Figure 1* shows the heat-up curves obtained in the oven used. A thermocouple was placed in the vinyl layer to obtain the results as shown. The coating thickness in these experiments is relatively high in order to facilitate temperature measurements. The 1.2 mm (47 mils) coating heated-up in about 2 min. The heat-up times are seen to be approximately proportional to the thickness of the coatings with reasonable precision. This is in agreement with *Eq 1*. From the curves a value for the heat transfer coefficient k can be calculated, using *Eq 1*. Values of around 40 J/(m²) (s) (°C) are found at maximum air

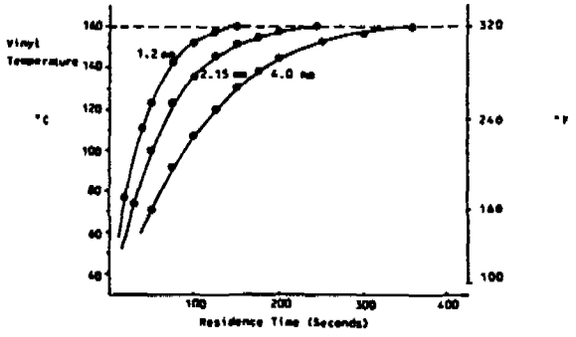

Fig. 1. Heat-up curves for different coating thicknesses. DINP-plastisol; oven temperature 160°C (320°F); 1.2 mm = 47 mils, 2.15 mm = 85 mils, 4.0 mm = 157 mils.

circulation rates. This range is also representative of industrial ovens. Overall, it appears that the test-assembly approaches real-life conditions well. Further experimental results will be described in the following sections.

SOME PRACTICAL RESULTS

The results shown below all refer to basic plastisol formulations: PVC 100, plasticizer 50 (DOP) or 53 (DINP) or 55 (DIDP), organotin stabilizer 0.5.

Exposure time is 2 min, unless otherwise mentioned. The coating thickness is 0.25 mm (10 mils), unless otherwise mentioned. Since the evaporation process is largely surface-determined, the results have been expressed in terms of weight loss per unit of time and area.

Influence of Plasticizer Type and Temperature on Process Volatility

Figure 2 reveals the profound influence of plasticizer type. Also the temperature dependence of the volatility is considerable: approximately 4% per °C or a factor 1.5 per 10°C (2.2% per °F or a factor 1.25 per 10°F). Still, at 200°C (392°F), DIDP has lower losses than DOP at 180°C (356°F).

The absolute level of the evaporation losses is high. For DOP at 200°C (392°F), for example, 8.7 g/(m²) (min) or 0.8 g/(ft²) (min) has been found. For a 1.8 × 18 m (6 × 60 ft) oven, having 32 m² (360 ft²) exposed vinyl surface, this means 360 × 0.8 = 290 g/min of DOP evaporated (max.), equivalent to 17 kg/h or 38 lb/h. Since the product is at lower temperature during the heat-up period, the calculated loss represents a high figure. Nevertheless, the calculated loss is in good agreement with the loss data shown in *Table 1*.

The relative process volatility DOP/DINP/DIDP is approximately 1/0.55/0.35. It is interesting to note that this ratio also holds for the vapour pressure of these plasticizers in the temperature range 350-400°F. This observation strongly suggests a direct relationship between process volatility and vapour pressure.

Influence of Coating Thickness and Exposure Time

The influence of coating thickness is mainly through longer required heat-up time. The apparent absolute weight loss over the same exposure period is slightly lower for thick layers than for thinner ones, due to the lower average temperatures at the beginning of the exposure period. *Figure 3* shows plots of the observed cumulative weight loss vs exposure time, for two plasticizers and for two different coating thicknesses. The weight loss for the thicker layers lags initially but parallels the curves for the thin layers after heat-up has been achieved. Thus, plasticizer evaporation is essentially surface-controlled since the thickness of the layer does not have an influence (apart from the initial lag). Another effect is noticeable from

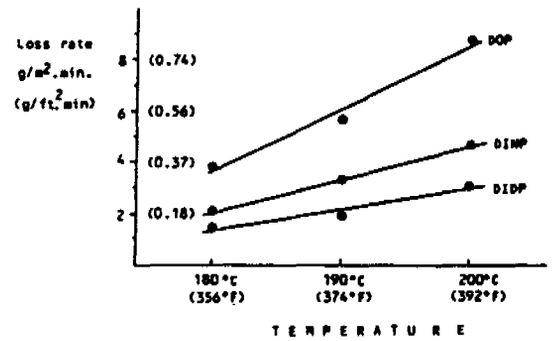

Fig. 2. Loss rates at different temperatures (0.25 mm coating thickness). Each point is the average of at least two test results.

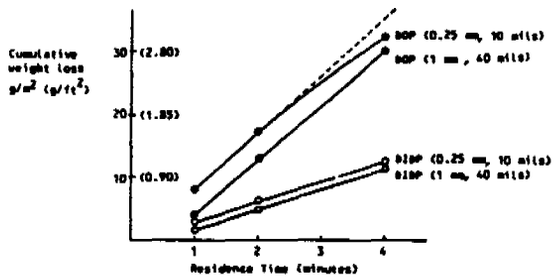

Fig. 3. Cumulative weight loss vs time for different coating thickness.

Fig. 3. The curve for DOP (0.25 mm, 10 mils), starts dropping off after 2-3 min. This is probably due to depletion of the plasticizer in the vinyl layer. The average loss rate for DOP is 8.7 g/(m²) (min) or 0.8 g/(ft²) (min). For a 0.25 mm (10 mils) coating—weighing approximately 300 g/m² or 28 g/ft²—this means 2.9 percent weight loss per min, or 8.7 percent of the plasticizer lost per min. Thus, after 3 min, approximately 25 percent of the DOP has evaporated from the sample. This is visible in the curve for DOP (0.25 mm). The depletion rate of the thicker layer is less on a percentage basis, of course, while the absolute loss rates (g/ft²) are closely similar.

Influence of Air Circulation Rate

The air circulation rate in the oven as used can be varied between 500 and 1400 m³/h (17,500-50,000 SCF/h). In most experiments the maximal rate has been used, obtaining conditions representative for industrial practice. Some experiments have been made at the minimum rate. The loss rates appear to be reduced to approximately half of thos at maximum rates. Also, temperatures have been recorded for the two cases. *Figure 4* shows the data for DINP. It is clear that a low air rate leads to slow heat-up. The loss rates are also considerably reduced. It is also clear, however, that the longer residence time required counteracts this lower loss rate.

CONCLUSIONS

The described technique to study process volatility—using a laboratory oven with considerable air convection, comparable to industrial

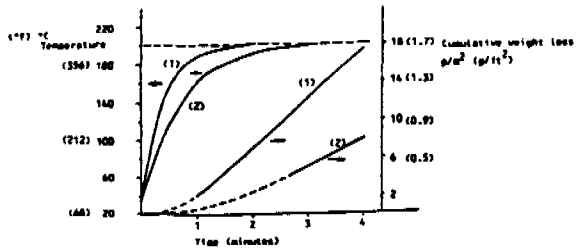

Fig. 4. Influence of air circulation rate (high = 1, low = 2) on heat-up and weight loss. DINP plastisol, 1 mm (40 mils).

practice—yields useful data otherwise not easily available. The influence of plasticizer type, temperature, and other factors can be investigated in a simple way.

The relevance of these experiments to real-life performance is obvious. By judicious choice of the plasticizer system, money can be saved and environmental measures be facilitated.

REFERENCES

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3. A. C. Poppe, *Kunststoffe*, 70, 38 (1980).