Studies on the Thermal Ageing of Organic Coatings

Ute Holzhausen[1)], *Dr. Sieghard Millow*[1)], *Prof. Dr. H.-J. P. Adler*[2)]

1) Institut für Lacke und Farben e.V., Magdeburg, (Institute for Varnishes and Paints, incorporated society), Germany

2) Dresden University of Technology, Institute of Macromolecular Chemistry and Textile Chemistry, Dresden, Germany

Summary: The ageing of organic protective coatings depends on environmental impacts and is associated with a variety of ichemical and physical processes. The results of former thermal ageing studies indicate that evaporation and polymer degradation are the decisive processes for changes in coating properties.

For the verification of these assumptions the impact of

- the thermal exposure temperature T_L and
- the length of the exposure time t_L

on properties of clear lacquer coatings was determined by further studies.

The gradation of T_L was aimed at creating conditions where on the one hand only evaporation processes occur, while on the other hand evaporation and polymer degradation reactions occur in parallel. The objective was to find the time t_L and the temperature T_L at which degradation starts to prevail.

1 Introduction

The durability and service life of coatings is limited mainly by ageing. During ageing, a large number of irreversible physical and chemical processes such as the diffusion, migration and evaporation of softening plasticizing substances, as well as post-polymerization, post-linkage, autoxidation, polymer degradation, relaxation and post-crystallization can occur, which are largely dependent on environmental factors. These ageing processes manifest themselves in a number of different ways. Despite the large volume of research which has already been carried out in this field, the processes which effect changes in the properties of coatings are still disputed, and the processes underlying ageing have still not been satisfactorily explained.

Earlier studies have found that almost all characteristic values and coating properties change during thermal exposure at 100°C in accordance with a logarithmic function in the form of equation 1-1 where the length of exposure is t_L (|1| - |9|).

$$\textbf{Characteristic value} = k * \ln t_L + c \qquad \textbf{eq. 1-1}$$

(where k and c are empirically determined constants)

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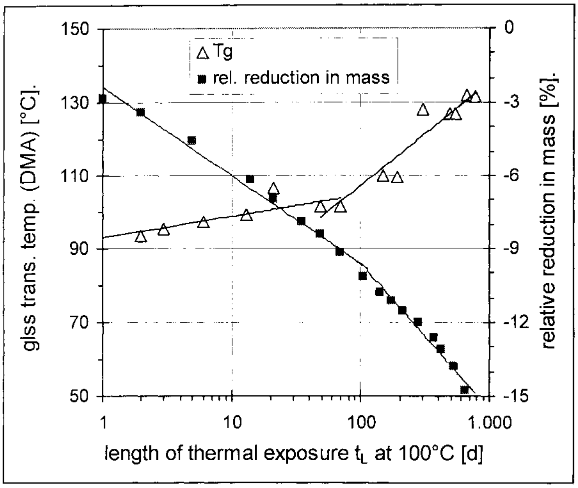

Figure 1-1: Tg-DMA and relative reductions in mass (gravimetrically determined) of a thermosetting, solventbased Acrylate-Melamine-coating in dependence on the length of exposure at 100°C

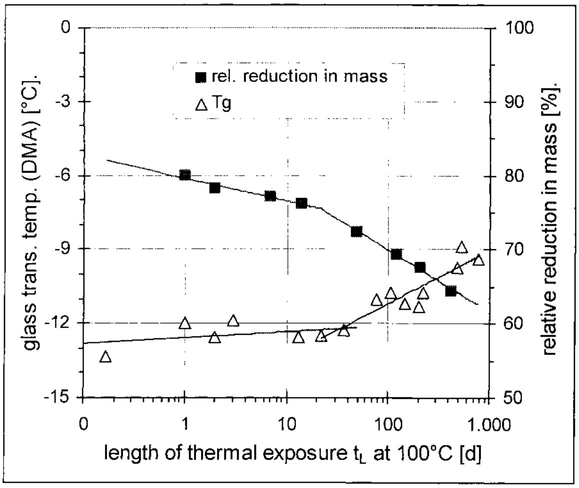

Figure 1-2: Tg-DMA and relative reductions in mass (gravimetrically determined) of a drying, waterbased Acrylate-dispersion-coating in dependence on the length of exposure at 100°C

Figures 1-1 and 1-2 summarize the values determined depending on length of exposure t_L for Tg (DMA), the glass transition temperature established by DMA, as well as those for the gravimetrically determined relative reductions in mass of two coatings with different binding agents, different curing/drying mechanisms and different solvents.

Closer examination revealed that at a certain point a change almost always occurred in the logarithmic function. The constant k acquired a different value. The changes were predominantly such that the properties or characteristic values changed more rapidly from this point on than they would have according to the old function.

The point at which the functional correlation changed depended primarily on the coating material (the binding agent), and less on the characteristic value or property being observed.

Further studies were aimed at identifying the causes underlying the changes in coating properties which were ascertained, and which were suspected in evaporation processes and in degradation processes of the polymer matrix.

2 Approach to a Solution

In order to establish the reasons behind the aforementioned changes in properties, external environmental factors were to be varied in such a way that ageing processes and phenomena could be ascribed to particular agents.One option was to select a number of graded thermal exposure temperatures ranging from ambient temperature to 140°C.

This gradation of thermal exposure temperatures T_L meant that the thermal energy recorded was either less than or greater than/equal to the activation energy for post-linkage or degradation processes. This would result either in evaporation processes alone, or in evaporation processes in parallel with post-linkage and/or polymer degradation reactions. This would then by necessity be reflected in a change in functional dependencies, for instance between Tg and the exposure temperature, and/or between internal stresses and the exposure temperature.

The studies had to be restricted to purely thermal loading, thus avoiding a parallel input of other forms of energy, as the effects of the graded energy input would otherwise have been masked.

3 Method

The characteristic values and properties of, for instance, water-dilutable clear varnish coatings were determined, as well as how they changed depending on length of exposure t_L and exposure temperature T_L. The following exposure temperatures T_L were selected: 25°C, 40°C, 60°C, 80°C, 100°C, 120°C and 140°C.

The *1st water-dilutable coating* was a 2K-PUR system (PUR-BS) which cures at room temperature. It was composed of the following principal elements:

- Binding agent: (parent component) based on an OH-functional polyacrylate resin (secondary),
- Curing agent: hydrophilic trimeric HDI,
- various auxiliary agents.

The *2nd water-dilutable coating* (AY-BS (wb)) was air-drying and was composed as follows:

- Binding agent component: styrene-acrylate copolymer emulsion,
- Film forming agent: butyl glycol,
- various auxiliary agents.

The changes in the coating properties caused by thermal exposure were established at various time intervals by:

- thermal analysis,
- radiometric tests,
- ATR-FTIR spectroscopy,
- gravimetric analyses and
- physico-technical examinations.

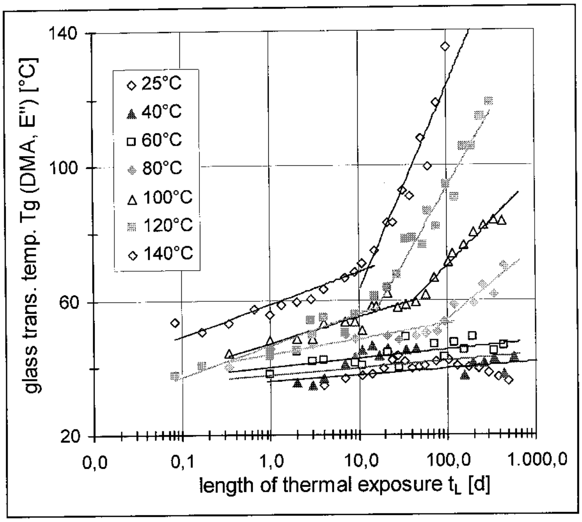

Figure 4.1-1: Glass transition temperature Tg-DMA of the coating PUR-BS in on the temperature and length of exposure

4 Results

4.1 Studies into thermal exposure of the PUR-BS coating

4.1.1 Determination of physical and mechanical properties

Since the glass transition temperature, one of the most important substantive coefficients of polymer materials, is very well suited to describing structural changes of the polymer matrix, particular importance was ascribed to it.

Figures 4.1-1 and 4.1-2 summarize the values established for the Tg (DMA) of the PUR-BS coating at different lengths of exposure t_L and exposure temperatures T_L, together with their correlations.

The glass transition temperatures of PUR-BS rise as thermal exposure increases. Both the Tg (DMA) and the Tg of the DSC analysis (not illustrated here) show a functional dependence of t_L in the form of equation 1-1. Whilst when T_L=25°C, 40°C and 60°C the functional dependencies between Tg (DMA) and t_L did not vary over the entire period of the study, when T_L=80°C, 100°C, 120°C and 140°C there was a change in the logarithmic function. In all four cases, the constant k acquired a greater value. The point at which this functional change occurred depended on exposure temperature T_L. For T_L=80°C, the functional change occurred after ca. 85 days. This change occurred considerably earlier, after ca. 43 days, at T_L=100°C. At exposure temperatures of 120°C and 140°C, these changes were observed even earlier, after ca. 16 days and ca. 13 days respectively.

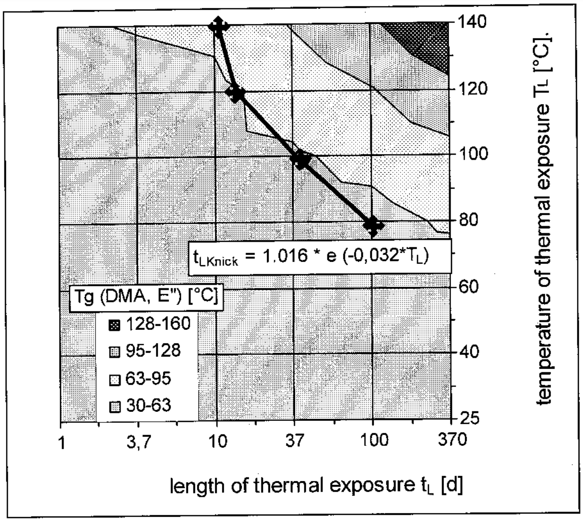

Figure 4.1-2: Correlation at the coating PUR-BS between the exposure temperature, the length of exposure and Tg (DMA) and respectively the functional change of Tg

Figure 4.1-2 is a graphic representation in the form of a 2D contour profile showing the correlations between Tg (DMA), the exposure temperature and the length of exposure. This also clearly demonstrates that Tg (DMA) is dependent on both T_L and t_L. Superimposed on the contour profiles is a line showing the dates when the functional correlation of Tg (DMA) changed for the respective exposure temperature. One can observe an exponential dependency in the general form of equation 4.1-1. between the point in time t_{LKnick}, at which the functional change occurs and a kink (*Knick*) appears in the curve, and exposure temperature T_L (the empirically determined function is also given in Figure 4.1-2).

$$t_{LKnick} = a * e^{-b*T_L} \qquad \textbf{eq. 4.1-1}$$

(where a and b are empirically determined constants)

As thermal exposure at lower temperatures increases in duration, the point of sudden functional change is displaced.

The degree of coincidence between the values of the exponentially determined function and the actual data is about 95%. Given this functional dependency, one cannot exclude the possibility that the change in the logarithmic function, the kink in the Tg (DMA) curve, might also be observed at temperatures of 60°C (after t_L≈615d).

The ATR-FTIR spectroscopic studies shed additional light on the degradation processes with PUR-BS. Depending on t_L and T_L, a clear reduction in the extinction of the absorption band of the NC oscillation of the urethane group could be recorded at 1531cm^{-1}. Figure 4.1-3 shows the curves of the relative extinction changes for the NC oscillation at exposure temperatures T_L=80°C and T_L=120°C.

It is significant that

- a linear functional dependency of the logarithm of exposure length was found, even for a relative reduction in extinction,

- at a point dependent on T_L, there is a change in the functional dependencies between the relative reduction in extinction and t_L, giving the curve a kink. This results in a change of function – similar to that observed with Tg (DMA) – such that the extinctions change more rapidly after the kink than they would do without this functional change.

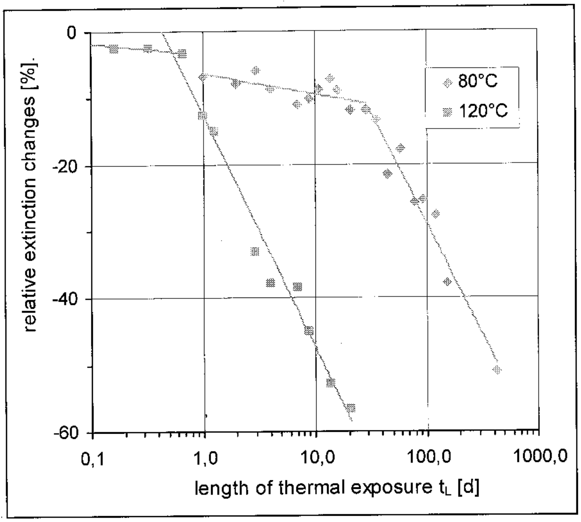

Figure 4.1-3: Relative extinction changes of the absorption band of the NC oscillation of the coating PUR-BS in dependence on the length of exposure at T_L=80°C and T_L=120°C

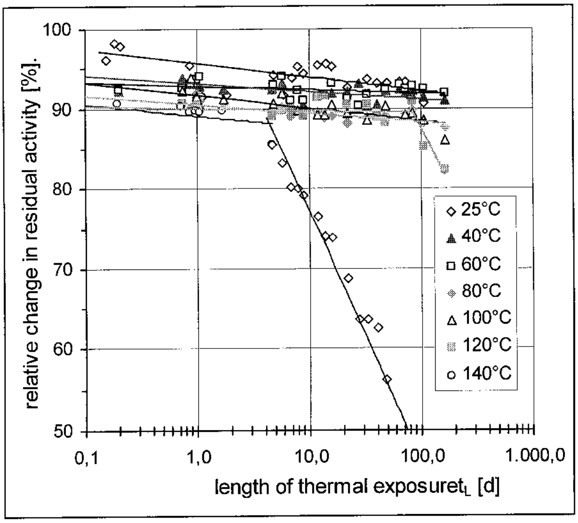

Figure 4.1-4: Relative C-14- residual activity of the coating PUR-BS in dependence on the temperature and length of exposure

At T_L=140°C the relative extinction changes were even greater, compared with those at T_L=120°C, resulting in the absorption band of the NC oscillation no longer being at all detectable after thermal exposure of 270d.

New absorption bands of functional groups or molecule skeletons formed during ageing were not detected, regardless of t_L und T_L. This suggests that the degradation process with PUR-BS coating occurs selectively with the formation of volatile products resulting from the decomposition of the urethane grouping. Low-molecular organic (e.g. amines) and inorganic (e.g. NH_3, CO_2) compounds would be conceivable. Characteristics similar to the Tg path were found when reducing the coating mass during thermal exposure.

The results of the retention of C-14 marked ethane-1,2-diol in PUR-BS show that the relative changes in residual activities, corresponding to the pulses per second calibrated on the coating masses, of PUR-BS were constant throughout the entire period of the study, taking into account measured value variations, with the exception of samples exposed to temperatures of 140°C and 120°C. It is highly probable that the functional hydroxyl group of the C-14 marked ethane-1,2-diol reacted with the isocyanate curing agent to the urethane group, and that the ethane-1,2-diol was consequently incorporated in the network through chemical bonding. This is supported by the high relative residual activities of ≈92%, which are above average for this study in our experience (and correspond to pulse rates of 11,000 pulses/s * g), the non-dependence on the temperature and length of exposure and the small reduction in relative residual activities observed in particular towards the beginning of thermal exposure in the period from 0.01d (15 min) to 0.1d (140 min) (Figure 4.1-4).

As already mentioned, a change in the functional correlation between the relative residual activity (calibrated pulse rate) and t_L was recorded for PUR-BS after ca. 4 to 5 days at T_L=140°C and after ca. 85d at T_L=120°C. From this point on, the values for the residual activity changed more rapidly in accordance with a logarithmic function of the form of equation 1-1. This functional change is probably due to polymer degradation.

One must qualify this, however, by allowing for the fact that the chemical composition of the PUR-BS samples for the retention studies and those of the samples for the other studies are not identical, because the dihydric alcohol ethane-1,2-diol formed a constituent part of the network. This can lead to a difference in thermal stability.

Studies of C-14 marked PUR-BS samples aged at temperatures of 25°C, 40°C, 60°C, 80°C, 100°C and 120°C did not show any evidence of the growing dominance of polymer degradation processes relating to the C-14 ethyl ester grouping up to an exposure length of ca. 120 days.

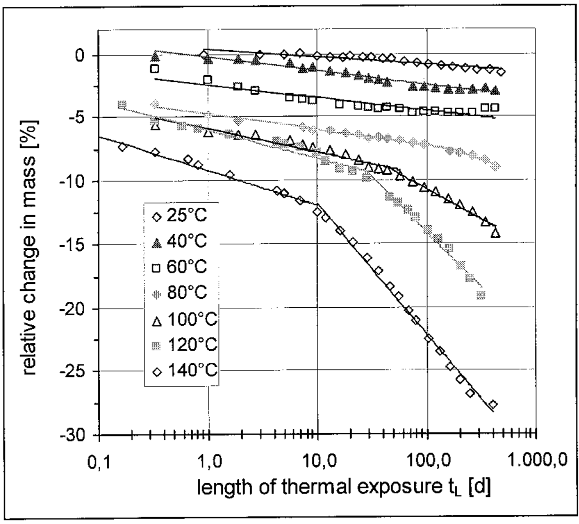

Figure 4.1-5: Relative reductions in mass (gravimetrically determined) of the coating PUR-BS in dependence on the temperature and length of exposure

Behaviour which was similar in particular to the DMA-Tg path was found when the coating mass was reduced during thermal exposure.

The results of the gravimetric mass analyses in Figure 4.1-5 show that the reduction in mass also proceeded in accordance with the general logarithmic function set up in equation 1-1.

The functional correlation between the reduction of the coating mass and the length of thermal exposure did not change at exposure temperatures of $T_L \leq 60°C$, and changed only at temperatures of $T_L \geq 80°C$. In every case the constant k again acquired a higher value when the function changed.

The high relative reductions in mass of more than 20% at exposure temperatures of 120°C and 140°C cannot merely be explained by the release of the solvent and of the auxiliary agents. This gives added weight to the suspicion that highly volatile polymer degradation products had already formed and been released.

The rise in Tg and the formation or increase of internal stresses (self-contained stresses) are also closely related in the case of PUR-BS (see Figure 4.1-6).

Whilst at exposure temperatures T_L=25°C, 40°C and 60°C the diminution in volume which accompanies the reduction in mass could be compensated for by flow processes to the extent that expansive internal stresses even built up in one phase of thermal exposure (over the entire period of the study at 25°C, and up to $t_L \approx 100$d at 40°C and up to $t_L \approx 30$d at 60°C), this phenomenon could no longer be observed at temperatures T_L greater than or equal to 80°C. At these temperatures contractive internal stresses built up in the PUR-BS coating as the Tg rose. The point at which contractive internal stresses begin to build up depends on the exposure temperature in the case of PUR-BS too.

The rise in Tg, the build-up or increase of contractive internal stresses and in particular the reduction in extinction of the absorption band of the NC oscillation of the urethane group lead one to anticipate increasing embrittlement or increased hardness of the PUR-BS in the course of thermal exposure and depending on the temperature. Figure 4.1-7 exhibits the changes in the mechanical coating characteristic Erichsen cupping, in relation to the length and temperature of exposure.

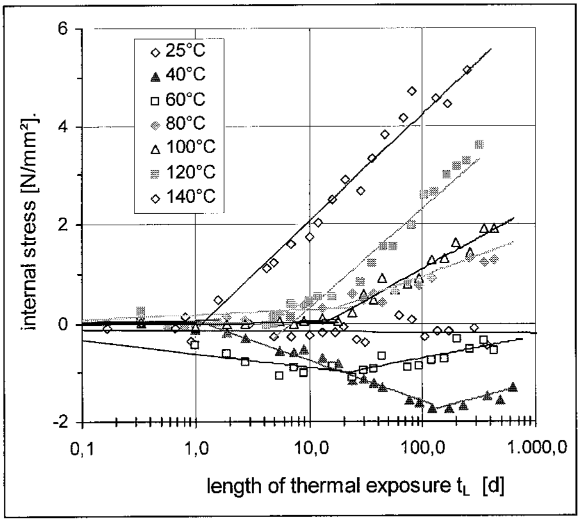

Figure 4.1-6: Internal stresses (IS) of the coating PUR-BS in dependence on the temperature and length of exposure

The cupping values are almost constant at temperatures of 25°C, 40°C and 60°C during the period of the thermal exposure study. At $T_L \geq 80°C$ the coating becomes less flexible and more brittle. The points in time at which this property changes are also dependent on exposure temperature and correlate well with those from the ATR-FTIR spectral analysis (t_{LKnick} at 80°C ca. 25d to 30d, t_{LKnick} at 100°C

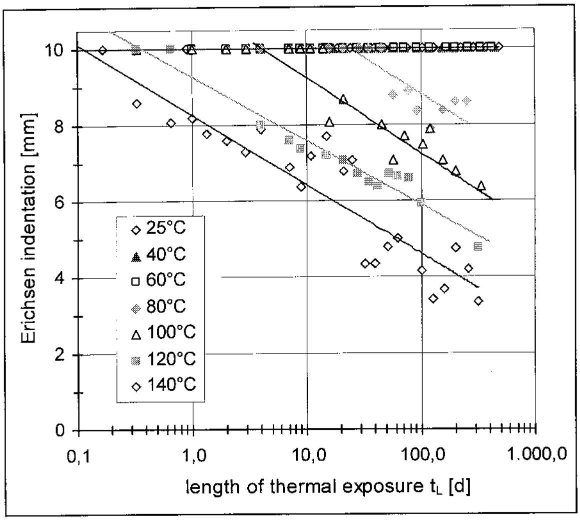

Figure 4.1-7: Erichsen indentation values of the coating PUR-BS in dependence on the temperature and length of exposure

ca. 4d to 5d, t_{LKnick} at 120°C ≈10h and t_{LKnick} at 120°C ≈3h). Like all the other characteristic values of PUR-BS, the cupping values during thermal exposure also change in accordance with a logarithmic function of the form of equation 1-1. The values of constants k at $T_L \geq 80°C$ are again almost exactly identical; they average out at 0.81.

The damage sustained by PUR-BS in the case of a rapid, discontinuous loading, such as that to which the coating is subjected during the impact test, was again dependent on the temperature and length of exposure. The resistance of the coating to cracking under impact-generated deformation was very high and almost constant over the entire period of thermal exposure at T_L=25°C, 40°C and 60°C (drop height 95 cm – 100 cm).

As with the results of Erichsen's cupping test, the coating became less elastic at exposure temperatures greater than or equal to 80°C, with cracking under impact-generated deformation.

4.2 Studies into thermal exposure of the AY-BS coating

4.2.1 Determination of physical and mechanical properties

Thermo-analytical studies into thermal exposure of the AY-BS coating, which is based on a styrene acrylate copolymer emulsion, showed that thermal exposure again led to an increase in Tg values. As found previously with the PUR-BS coating, the Tg changes with AY-BS also follow a logarithmic function of the type of equation 1-1.

It is striking that a change in the function only occurs again at a temperature of 100°C or above, and at a relatively late point in time (after ca. 105d, after ca. 35d at 120°C and after ca. 20d at 140°C) (*Figure 4.2-1)*. From this point on, the changes in the Tg values are again greater than they would be according to the previous function. These functional changes in the Tg path were again recorded simultaneously with the DMA analysis and almost simultaneously with the DSC analysis. As with PUR-BS, the appearance of this functional change was dependent on both the length of exposure and the exposure temperature.

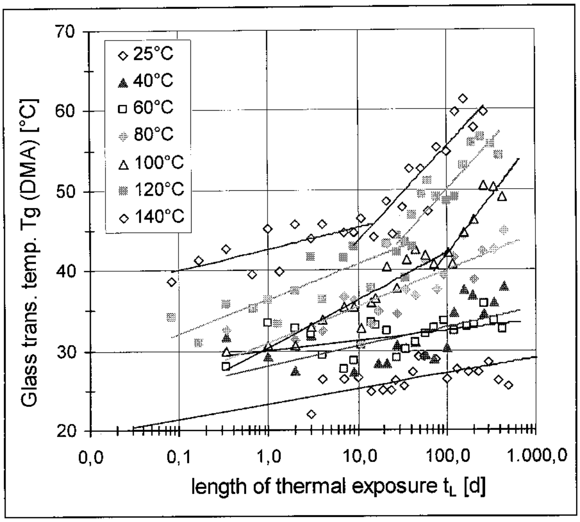

Figure 4.2-1: Glass transition temperature Tg-DMA of the coating AY-BS in dependence on the temperature and length of exposure

The results on the retention of C-14 marked ethane-1,2-diol in AY-BS show that the pulse rates of AY-BS calibrated on the coating mass, the residual activities, are logarithmically dependent on the length of exposure. At the beginning of thermal exposure, in the period from 0.01d (15 min) to 1d, a sharp drop in residual activities was recorded depending on the temperature, and was ascribed to the phase of film formation (drying). This phase is completed after ca. 1-2 days' exposure at T_L=25°C, after ca. 5 hours at T_L=40°C, after ca. 2.5 hours at T_L=60°C, after ca. 2.5 hours at T_L=80°C, after ca. 45 minutes at T_L=100°C and within the first fifteen minutes at T_L=120°C and T_L=140°C.

The end of the drying phase is marked by residual activities in the region of 250 to 350 pulses/s per gram AY-BS.

Surprisingly enough, a change in the functional correlation for the residual activities of AY-BS depending on t_L at T_L≥80°C was also recorded. In every case the constant k acquired a greater value, i.e. the diffusion and evaporation of the C-14 marked ethane-1,2-diol occurred more rapidly from this point onwards (the point at which the kink appears in the curve) than would have been the case with the previous old function (Figure 4.2-2). The kink appeared after ca. 15 days at T_L=140°C, after ca. 20 days at T_L=120°C, after ca. 22 to 25 days at T_L=100°C and after ca. 28 to 30 days at T_L=80°C. The cause of this functional change could

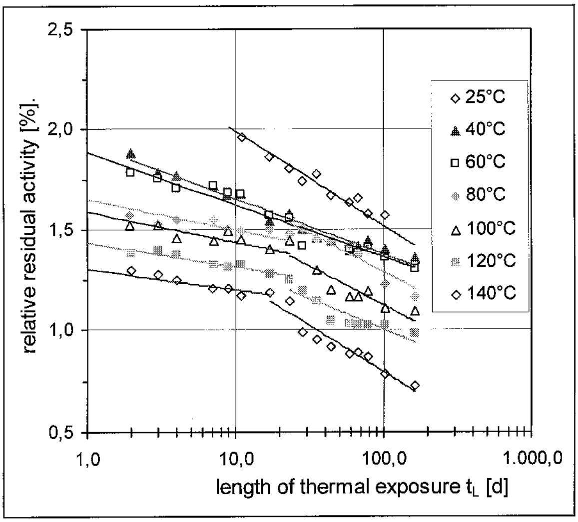

Figure 4.2-2: Relative C-14- residual activity of the coating AY-BS in dependence on the temperature and length of exposure

not be determined. One suspects that chemical and/or structural changes in AY-BS favour the diffusion and evaporation of ethane-1,2-diol.

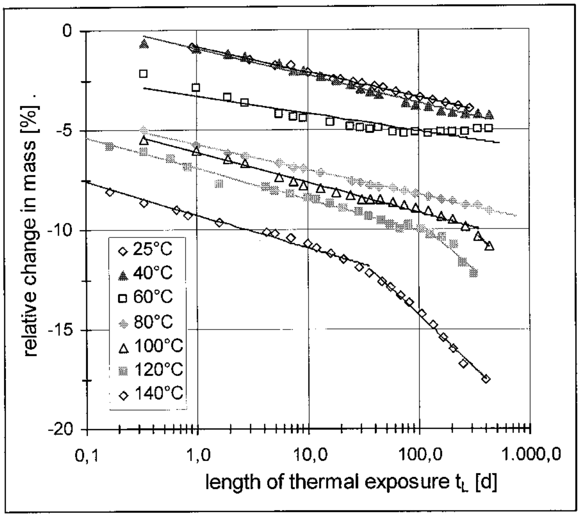

Figure 4.2-3: Relative reduction in mass (gravimetrically determined) of the coating AY-BS in dependence on the temperature and length of exposure

Figure 4.2-3 exhibits the values of the gravimetrically determined relative reduction in mass of AY-BS, related to the mass of the coating following conditioning under ambient conditions. This demonstrates that the functional dependencies between the reduction in mass and the length of exposure change in the course of thermal exposure at temperatures equal to or exceeding 100°C. The points at which these changes occur almost coincide with those for the glass transition temperature, and are equally dependent on the length and temperature of exposure.

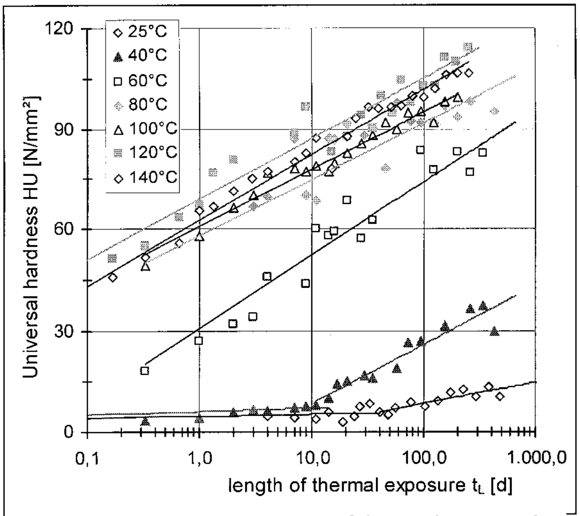

Figure 4.2-4: Universal hardness of the coating AY-BS in dependence on the temperature and length of exposure

The smaller changes in Tg values in comparison with PUR-BS, the later build-up and smaller increase in contractive internal stresses and the relatively small loss in mass of no more than 17 % lead one to expect evidence of embrittlement appearing later in AY-BS during thermal exposure. This was confirmed by Erichsen's cupping values. These showed that the coating retained a constant high level of flexibility throughout the entire period of the study regardless of the length and temperature of exposure.

As might have been anticipated, the characteristic values of pendulum hardness (attenuation 'hardness') and universal hardness (HU) also exhibited a functional dependence on the temperature and duration of exposure in accordance with a logarithmic function (from 60d at T_L= 25°C and from 12d at T_L=40°C). But surprisingly, no changes in functional correlations occurred in the period of the study.

The value of the constants k of all logarithmic functions determined for HU was of about the same magnitude from $t_L \approx 12$d (*Figure 4.2-4).*

5 Summary and Evaluation of Results

The most important findings from the results presented are as follows:

All characteristic values of the coatings included in the study, and not just the glass transition temperature Tg, change, independently of the mechanism of film formation and of the binding agent and solvent base, according to the length of thermal exposure t_L in accordance with a logarithmic function of the following form:

$$\textit{Characteristic value} = k * \ln\ t_L + c \qquad \textbf{eq. 5-1}$$

(where k and c are empirically determined constants)

Their rates of change thus become increasingly small.

In the logarithmic time-scale, changes in these logarithmic functions occur for many characteristic values, depending on exposure temperature T_L and length of exposure t_L; the values of k and c change without transition. This gives the curves a kink. A typical curve consists of two curve branches which constantly merge.

The new functions are predominantly such that an acceleration in the change of characteristic values occurs in relation to the previous function, and the characteristic values and properties deteriorate more rapidly.

Functional change is dependent not only upon T_L and t_L as stated above, but also upon the binding agent of the coating.

The functional change occurs for all characteristic values of a binding agent at the same exposure temperature after about the same length of exposure, leading one to suppose that there must be a common cause for this. As the values change spasmodically with the exposure temperature, we are very probably dealing here with temperature dependent reactions, suggesting that new chemical reactions are taking place.

There often exists between the length of exposure t_{LKnick}, the point at which a kink occurs in the curve, and the exposure temperature T_L a functional dependency of the following exponential function

$$t_{LKnick} = a * e^{-b*T_L} \qquad \text{eq. 5-2}$$

(where a und b are empirically determined constants).

One can conclude from these results that physical and chemical ageing processes lead to embrittlement and the formation of internal stresses in organic surface protective coatings.

With studies depending on the length and temperature of exposure, the first appearance of a kink in the curve of a characteristic value indicates a greater dominance of chemical ageing processes at these and higher exposure temperatures.

At exposure temperatures where there is no functional change, physical ageing processes predominate. These are caused primarily by evaporation of low-molecular coating components.

It is especially significant that, contrary to the assumption made by the Arrhenius equation on activation energy, the introduction of new chemical degradative reactions is not only dependent on temperature, but also on time.

A knowledge of the functions for changing characteristic values might form the basis of an assured and effective assessment of the long-term characteristics of coatings, because it has been shown that the value of the constants in the logarithm function is dependent on the characteristic value, and in many cases is of an equal magnitude both before and after the kink for all temperatures to which a coating is exposed.

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