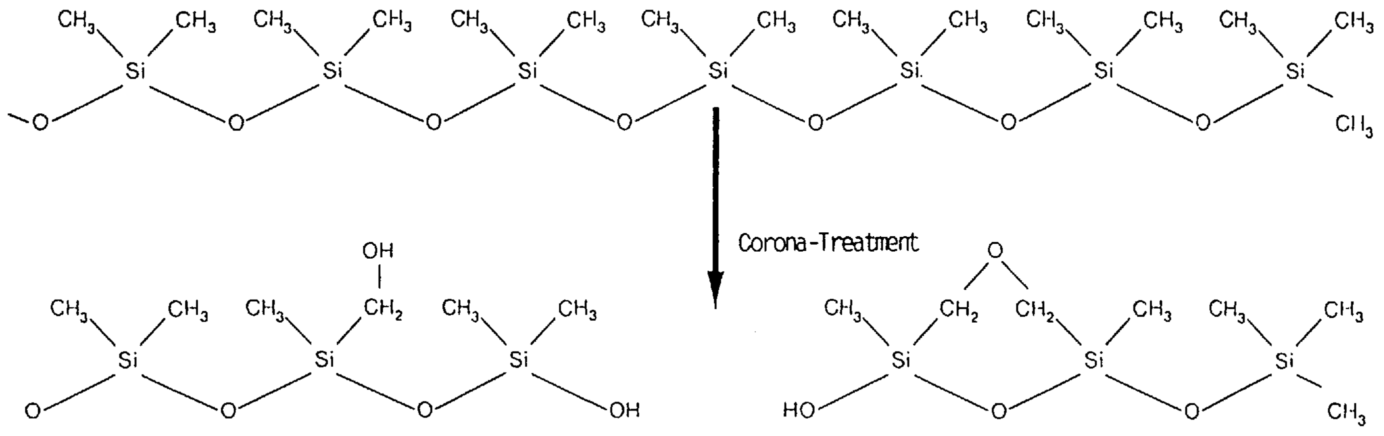

Fig. 13. *Effect of the corona treatment on the structure of polydimethylsiloxane*

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Explanations

Our examinations of the paint surfaces before and after the ETA treatment by means of IR spectrometry, electron microscopy, and ESCA-analysis have shown chemical changes in a few molecular surface layers of the top coat to be responsible for the adhesive effect. As expected, the oxygen content of the layers increased through the corona treatment, but the even bigger increase in nitrogen due to surface nitration by formation of nitric oxides was unexpected and astonishing. In *Fig. 10* the changing amounts of silicon, nitrogen, oxygen, and carbon before and after the corona treatment are displayed. The oxygen increase due to the corona treatment is between 10 and 20%, whereas the nitrogen content increases by 40 to 100% depending on the paint system. To get a better picture an Ar ion etching on the corona treated surface has been carried out (*Fig. 11*). This etching process is able to level off the very top nanometers of the surface and thus may reveal the order of the nitrated layers. By the Ar etch in this case, an approximate layer of 20 nanometers was carried away. Therefore we can estimate the modified surface layer thickness to be of the order of 50–60 nanomters.

It is also remarkable to note that, through the corona treatment, silicon additives on the surface are partly changed to adhesion-compatible oxidised products and partly degraded to volatile fragments. In *Fig. 12*, the effect of corona treatment on the surface of polydimethylsiloxane is illustrated by the changing amount of silicon, oxygen, and carbon in the very top surface layers measured by IR spectroscopy. The change of the molecular structure of the polydimethylsiloxane into hydroxymethyl-, hydroxy- and ether-group-containing siloxanes was determined by ESCA analysis and illustrated in *Fig. 13*.

Summary

Through the corona treatment, adhesion resistant top coats become adhesion-compatible substrates for polyurethane adhesives. This reliable, purely physical process which can be automated, replaces the expensive, manual, wet pretreatment using body primers containing solvents which are inflammable.

Chimia 44 (1990) 326–336
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Recent Developments in the Field of Powder Coatings

Jean-Marie Loutz*

1. Introduction

In 1960, the first electrostatic spray experiments were carried out allowing the application of powder paint to cold and intricately shaped metallic objects. With this process, it is possible to apply films, with a thickness varying from 40 to 300 µm, in one single coat. At that date powders based on epoxy resins and dicyandiamide hardener were used in the functional coating field, *e.g.* for pipe protection. Due to photodegradation of bisphenol A based epoxies, leading to chalking and loss of gloss, there was a need to develop alternative mixtures of resins and cross-linkers for the decorative coating market.

Following the emergence of several possibilities to overcome the drawback, associated with bad weatherability, various directions were taken on the different continents. The USA and Canada chose the so-called polyurethane powders (in fact the urethane is made *in situ* from blocked isocyanate and hydroxylated polyester), because the dominant position of the automotive industry for which the flow of the paint is of prime importance. Japan opted for acrylic copolymers, recognized for their resistance to UV-induced degradation, containing glycidyl methacrylate which are cross-linked by means of long chain aliphatic diacids. Trials conducted with these systems failed in Europe either due to the volatile emission of caprolactam during baking or to poor mechanical proper-

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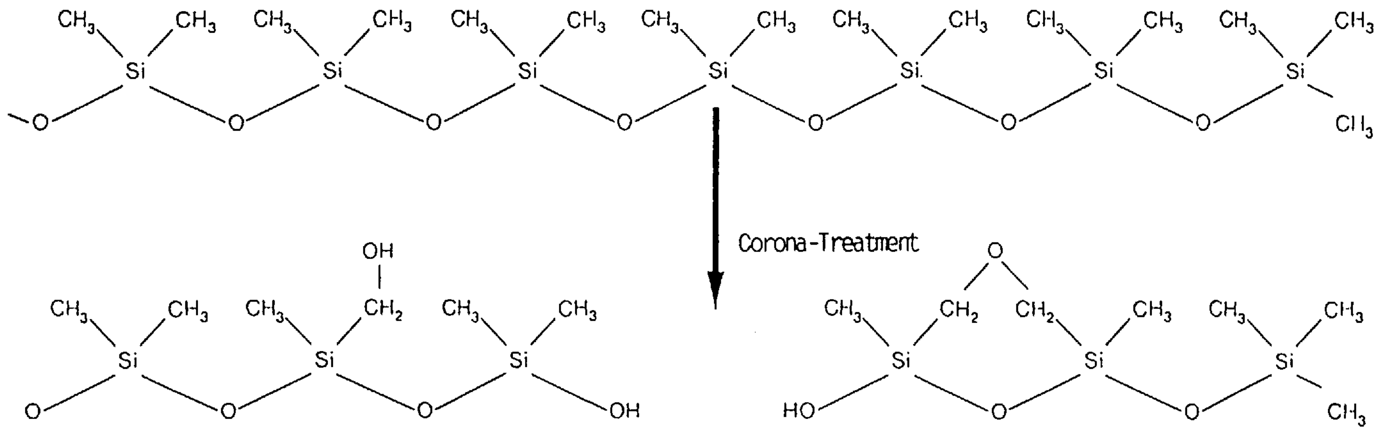

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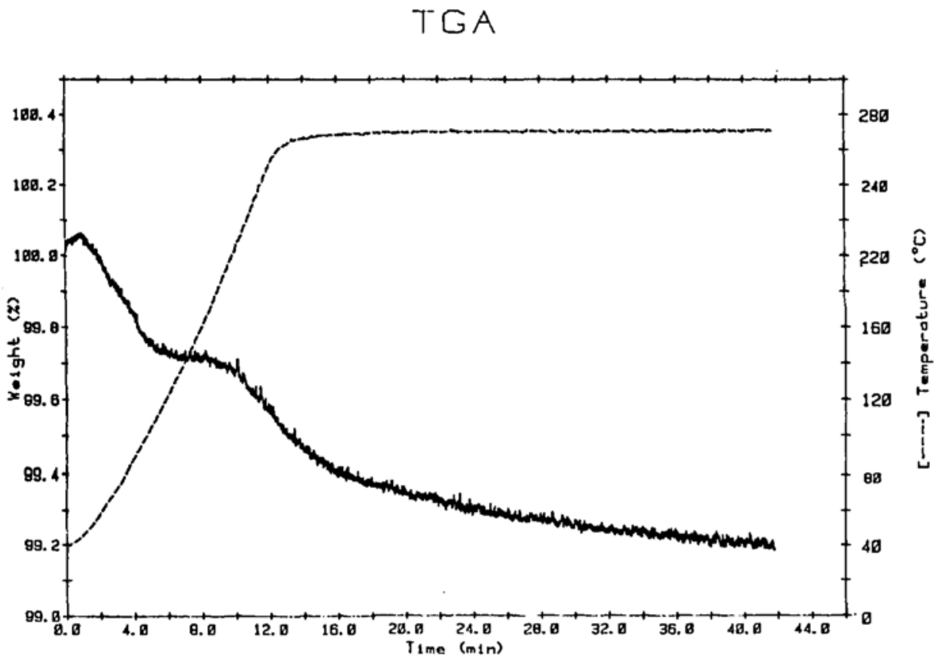


Fig. 1

ties and incompatibility problems. In Europe two companies, *UCB* in Belgium and *Unilever* in Holland, developed carboxy-terminated polyesters specifically designed in order to react with a unique solid aliphatic trifunctional epoxy (triglycidyl isocyanurate = TGIC) commercialized by *Ciba-Geigy* [1]. The good outdoor performance associated with high mechanical resistance against deformation of these paints explains, why over the last couple of decades powder coating has gained a significant market share of the metal protection and decoration activity. Apart from the quality of the solid polyesters-based paint, it is obvious that economic considerations (no waste, lower energy requirement: air is renewed twice an hour instead of 15 times for solvent paints) and the environmental friendly character (no solvent) are the strong driving forces resulting in the extended use of this technique.

A thermogravimetric diagram of a typical polyester-TGIC paint is shown in *Fig. 1*. A weight loss of 0.8% (mainly adsorbed water) is only noticeable after 40 min at 270°.

In 1989, the total European thermosetting powder coating consumption is estimated to 110,000 tons and 210,000 tons world-wide [2]. The average annual growth rate in consumption is extended to be 10–12% until 1996. In 1987, the market of powder coatings in Europe by weight of supplied industrial coatings on the whole was about 5.3% [3].

In this paper, we will restrict our comments to some characteristics and actual trends of the polyester-TGIC system which ranks for 17% of the total thermosetting powders market (*Fig. 2*).

2. Triglycidyl Isocyanurate

The ability of a thermosetting system to quickly achieve its maximum level of cross-linking density is important, because it determines the time-temperature parameters to be used, which influences the energy costs and the ability to paint heat sensitive substrates. Reactivity is dependent on numerous factors such as molecular weight of the resin, branching, concentration of reactive groups on the polymer backbone, nature and level of catalyst, reactivity and solubility of the cross-linking agent in the polyester.

It has been shown that commercial TGIC is made from a mixture of two diastereoisomers, and not allotropic structures, characterized by different melting points [4]. The ratio between the two isomers depends on the synthesis route and further purification which have been selected. The melting points of the two products are in the range of 103–104.5° and 156–157°, respectively, the latter being insoluble in boiling THF, can be easily isolated. Depending on the supplier the ratio between the 2 isomers can vary within rather large limits (*Table 1*).

Table 1

Supplier	A	B	C	D	E	F
High-melting-point compound [%]	4.3	1.7	9.0	9.3	18.9	9.0

Several triglycidyl isocyanurate mixtures manufactured in China are now available on the European market. It seems likely that the same producer is distributing its epoxy through different sales organisations.

During the manufacture of the paint the different components are mixed and sheared in an extruder at temperatures ranging from 90 to 130° but never as high as 160°. This means that, in some cases, substantially high quantity of the cross-linking agent will only act as an inert filler during extrusion. At baking temperatures, above 160°, some interaction may occur at the interface between the highly viscous liquid polyester and partially fused granules of TGIC. Due to the fast increase of viscosity during the network formation, complete diffusion of the melt TGIC is hindered. This is clearly noticeable in clear

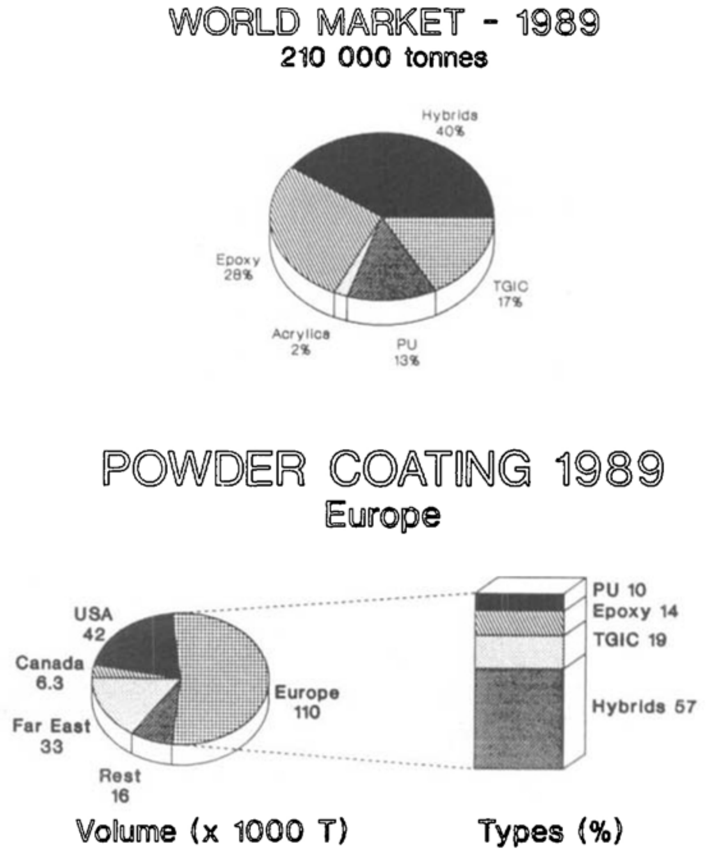


Fig. 2

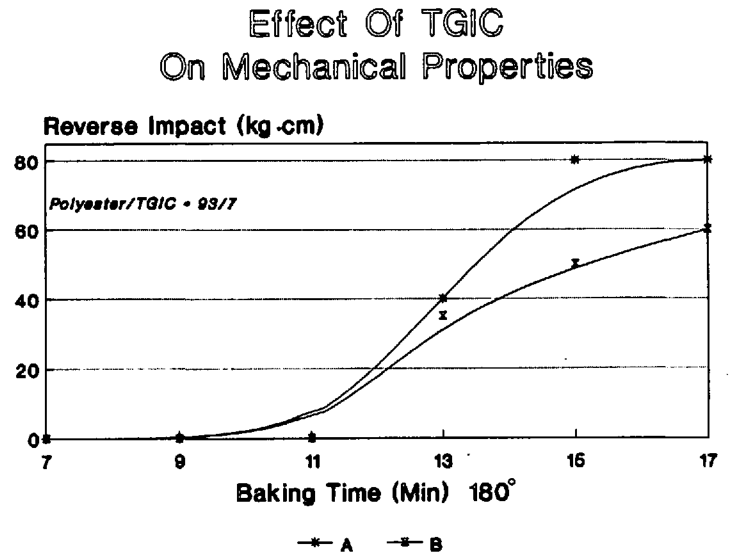


Fig. 3

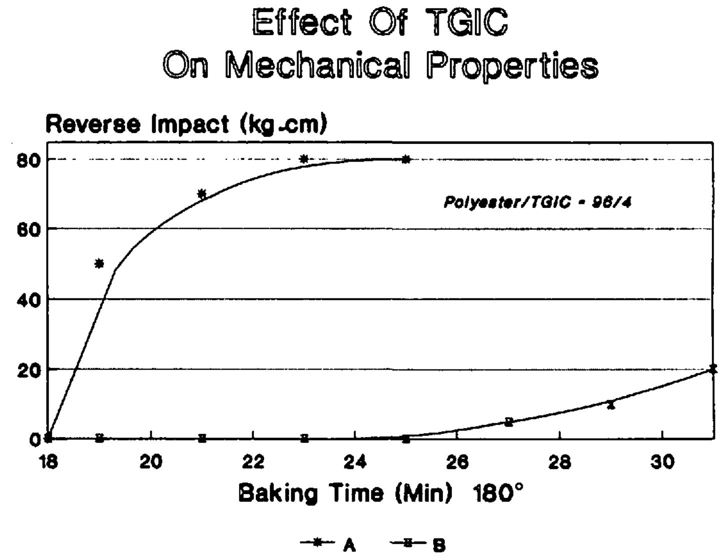


Fig. 4

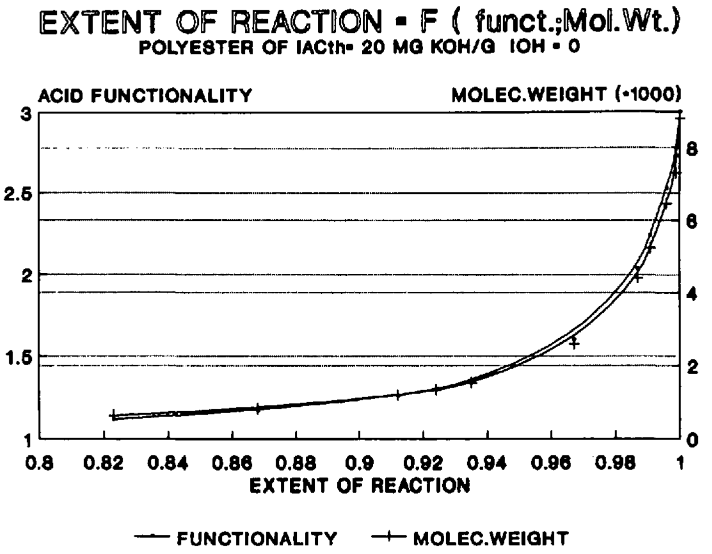


Fig. 5

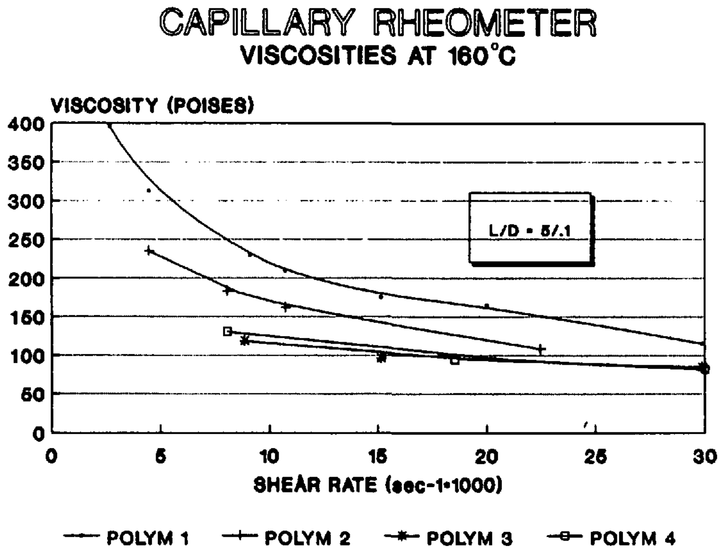


Fig. 6

varnishes in which small white crystals are seen under the microscope.

The mechanical properties of a polyester/TGIC powder paint are strongly influenced by the stoichiometric ratio between –COOH and $-\overset{\mathrm{O}}{\mathrm{C{-}C}}-$ groups. Paints have been made from the same polyester (acid value = 30 mg KOH/g) but with the two forms of TGIC (A: m.p. = 103°; B: m.p. = 156°), and the evolution of the impact resistance of the film with the curing time at 180° is visualized in *Fig. 3*. With a theoretical stoichiometry – COOH/epoxy ratio it is impossible to reach a level of direct impact resistance higher than 60 kg·cm with the high-melting-point isomer. The gel times of the powders at 180° are 135 and 210 s, respectively.

The situation is even more noticeable, if the polyester has a higher molecular weight (acid value = 20 mg KOH/g) and is designed to react with a lower amount of TGIC (weight ratio polyester/TGIC = 96/4). In this case, where a precise balance between reactive epoxy groups and homogeneity of the binder phase is critical, it appears that the low solubility of the B form makes the formation of a network impossible. Thus, the paint remains thermoplastic and brittle even after long baking time (*Fig. 4*).

3. Flow

To obtain a powder coating which exhibits the same surface appearance as a solvent based paint is a major goal for solid paint producers. The achievement of such objective is, however, the result of a compromise between required characteristics of the polyesters which are physically contradictory: high glass transition temperature (Tg), low-melt viscosity, slow network build up, high reactivity [5].

In powder coating, the unbaked powder is not forming a continuous layer and consists, at the application temperature, of solid particles whose dimensions are of the order of magnitude of the cured layer. There is no transient component allowing to adjust the levelling of the coating.

The Tg of the binder has a major influence on the physical stability of the powder. If the Tg would be lower than the storage temperature, the segmental mobility would be high enough to produce a considerable degree of interpenetration of the molecular chains belonging to adjacent powder particles, resulting in caking of the powder. Due to this practical constraint, it is impossible to reduce the Tg of the polyester below ± 50°. This affects the melt viscosity which is directly dependent on the Tg [6]. From a practical point of view, it means that a good storage stability must be associated to a high viscous binder.

The two following formulas are also well-known [7]:

$$X = X^{\infty} - \frac{A}{Mn}$$

$$\log\eta = \log \mathrm{Mw} + B$$

(for low-molecular-weight substances like polyester)

where X denotes a mechanical property like impact resistance

Mn	number average molecular weight
η	melt viscosity
Mw	mass average molecular weight
A, B	empirical constants

To obtain a satisfactory level of mechanical properties the level of molecular weight must be high enough, and this has a direct impact on the melt viscosity of the polyester.

To improve the reactivity of a polyester, that is its ability to develop quickly a three dimensional structure with a given cross-linker, it is possible to increase its functionality by introduction in its backbone, branching components such as trimethylolpropane.

Fig. 5 shows the evolution of functionality with the extent of the reaction of a polyester having a final acid value of 20 mg KOH/g (theoretical hydroxy value at the end of the reaction = 0). High functionality will consequently give a fast increase in melt viscosity and shorten the time available for the coating to flow during film formation. The result will be the obtaining of a rough surface with a strong orange peel effect.

It is obvious that during the last past years a lot of work has been carried out by resins and paint manufacturers in order to reduce the viscosity of the polyesters, not only to improve their flow properties for better appearance but also to obtain a better wetting of the substrate and increase the corrosion resistance [8]. This goal has been achieved by modifications of the polyester compositions, improvements in manufacturing process in order to obtain better reactive telechelic backbone allowing a reduction in the degree of branching, introduction of some degree of crystallinity in the polyester, and selection of catalyst having a more temperature-dependent efficiency allowing the fusion of the resin while it still remains in its thermoplastic stage.

In *Figs. 6* and *7* are shown the viscosity measured with a *Göttfert* capillary rheometer of old (Polym 1) and new generations of carboxylated polyesters having the same acid value = 30 mg KOH/g. Due to their lower viscosity at low shear rate and less pseudoplastic character, products like Polym 3 and 4 exhibit a much smoother surface appearance. It is interesting to note the spectacular reduction of viscosity at low temperature (120°) at which the reaction with TGIC has not started allowing a better spreading of the polyester before the start of the cross-linking.

Fig. 8 schematically depicts the viscosity-temperature history of these two types of polyesters during a baking cycle. Apart from the chemical composition, physical parameters such as particle-size distribution of the powder play an important role on the coating appearance, like what happens when a consolidated film is formed from an aqueous emulsion. A more uniform structure is obtained, when the mean diameter (R) of the solid particles is lower as expressed by the general equation.

$$t = \mathrm{f}\left(\frac{\eta R}{\gamma}\right)$$

where t is the time required for two particles to coalesce, η the viscosity and γ the surface tension [9].

Fig. 9 shows the particle-size distribution of the same paint which has been ground with an *Alpine UPZ 160* at 2800 rpm one and four times (feeding speed = 0.5 kg/min).

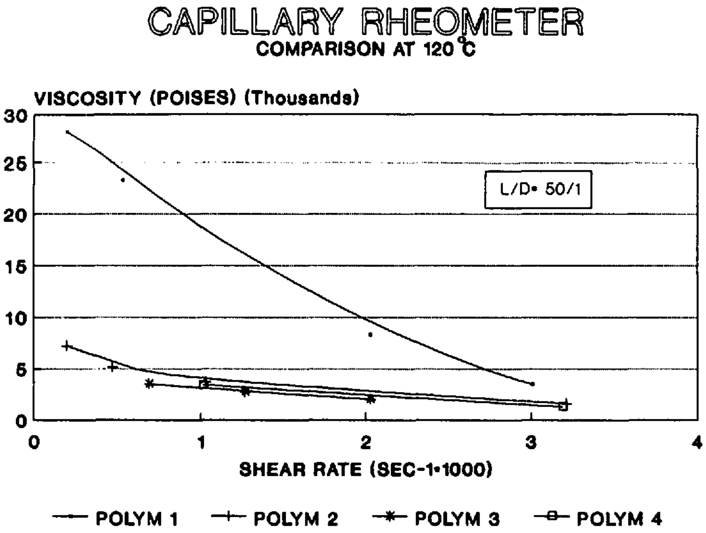


Fig. 7

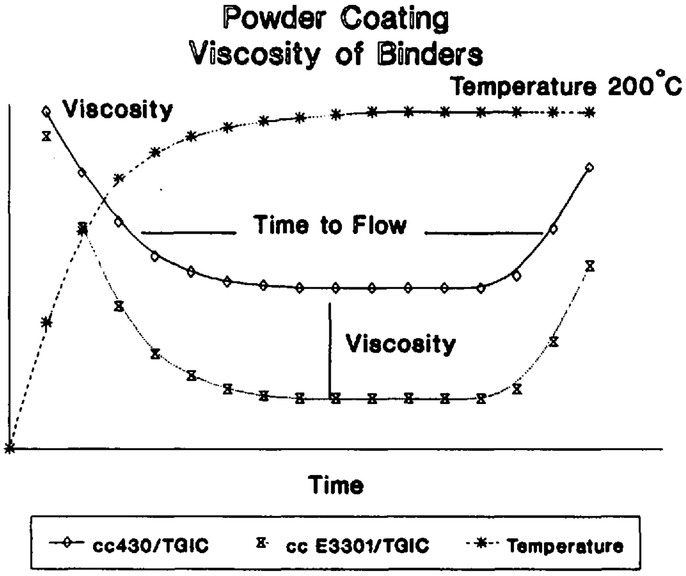


Fig. 8

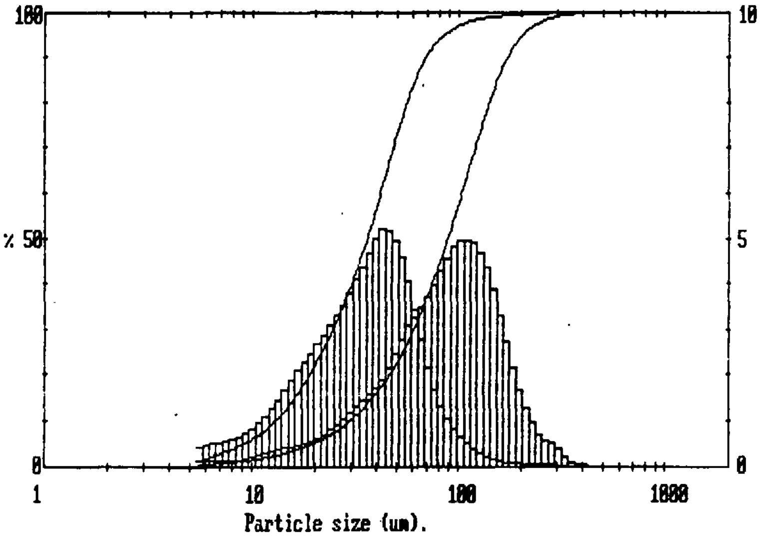


Fig. 9

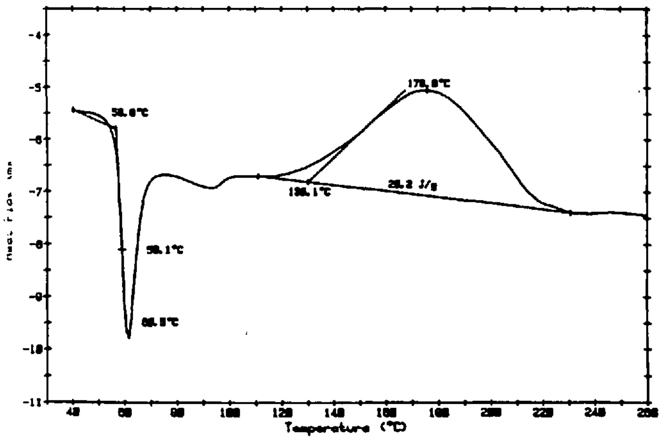


Fig. 10

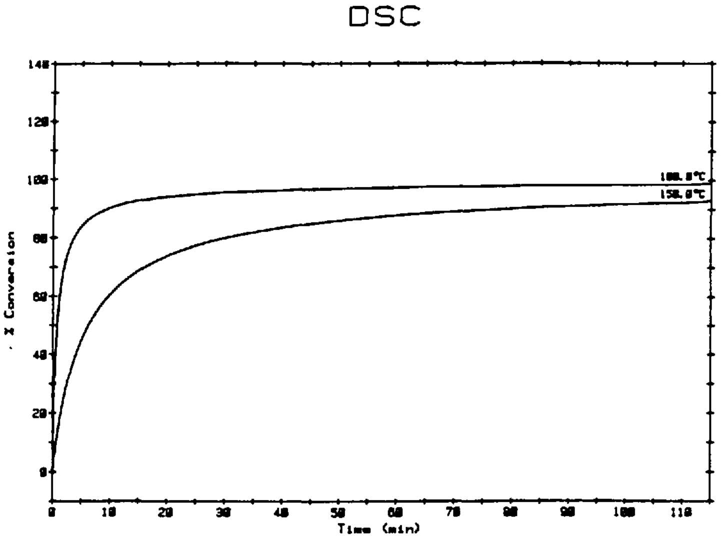


Fig. 11

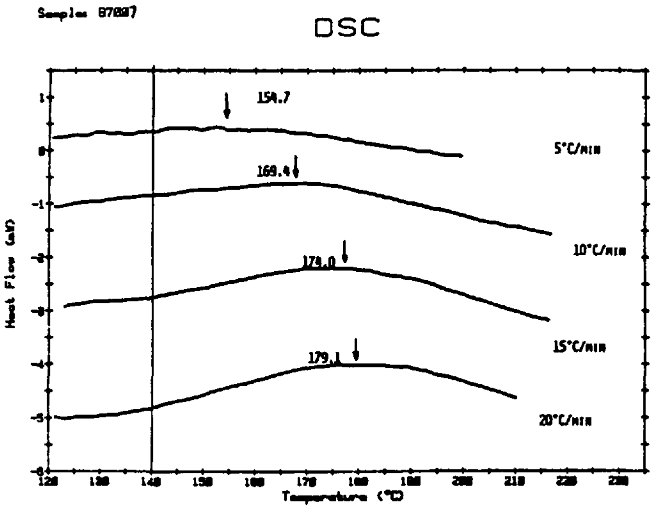


Fig. 12

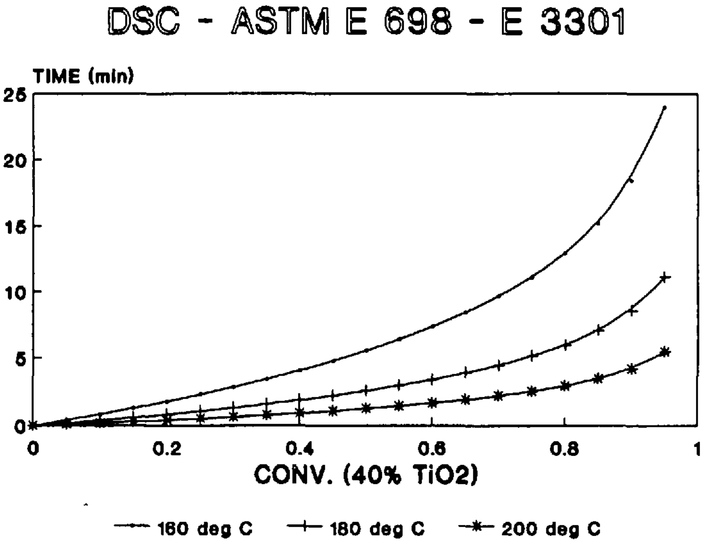


Fig. 13

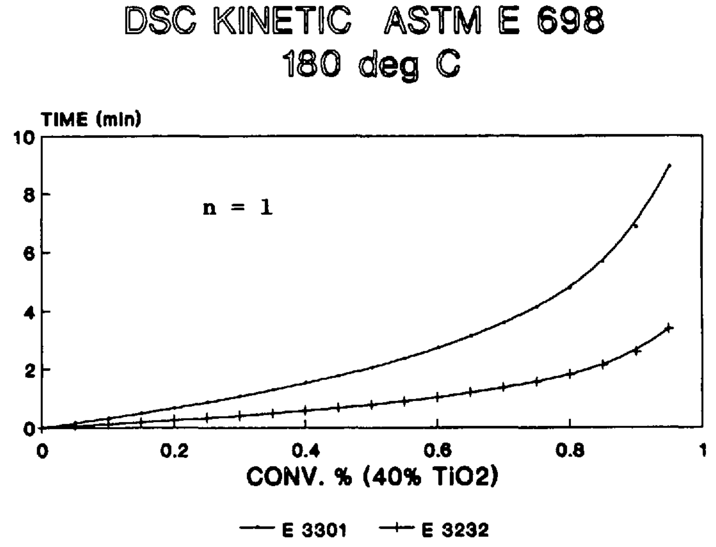


Fig. 14

As a result of more intensive milling, the mean particle size, measured with a *Malvern PS 64*, is reduced from 172 to 68 µm. The evolution of the surface smoothness of cured films obtained from these paints can be recorded with a *Diavite DT 100* micro probe which visualized the topography. For the powder ground at 172 µm, the mean thickness deviation between peaks and valleys is 1.27 µm, and the maximum difference in surface thickness is 6.9 µm; for the powder ground at 68 µm these respective values drop to 0.33 µm and 1.8 µm. These differences are macrospically noticeable, as the surface appearance visible to the naked eye changes from a strong orange peel structure to a smooth surface.

In powder coating and contrary to what happens with emulsions, there is no contribution of the capillary forces due to interstitial water. These forces being the determinant coalescing factor because fusion occurs when [10]:

$$G < \frac{266\,\gamma}{R}$$

G = elasticity modulus of the polymer
γ = surface tension of H_2O in the capillary

The H_2O content of powder stored, at room temperature, in open container during 6 months is less than 0.8%. Nevertheless, this absorption induces a spectacular drop of viscosity of about 10% which may be attributed to a reduction of strength of H-bonding between –OH and –COOH end groups and maybe to some hydrolysis.

In the process of film formation from powders, the main driving force is probably generated by the phenomenon of autoadhesion or mutual interdiffusion of free polymer chain ends across the particle-particle interface under the influence of the viscous flow of the melt polyester at the beginning of the baking cycle [11].

The surface tension of the paint works against the surface appearance of the coating. On one hand following the *Rhodes* and *Orchard* theory describing the formation in function of time of a continuous fused film from an irregular surface, it appears that a good levelling is related to high surface tension [6] [9]. On the other hand according to the *Young*'s equation, the interfacial tension between the fused coating and the substrate (γ sp) must be as low as possible in order to avoid the cratering effect.

From our experience it seems that the viscosity of the system and its evolution during the curing plays a much more critical role than a high γ on the orange peel effect. On the contrary, decreasing the value of γ is of prime importance in order to get an uniform wetting of the surface without formation of pinholes. In *Table 2*

Table 2

Trial	Coating	Binder	γd [mJ/m^2]	γnd [mJ/m^2]	γ [mJm^2]	Surface appear.
A	paint	1	44	2.1	46.1	orange peel
B	paint	2	44	2.3	46.3	smooth
C	paint	3	44	3.3	47.3	strong crater
D	paint	3	26	1.0	27.0	smooth
E	varnish	2	32	6.1	38.1	smooth
F	varnish	2	41	9.6	50.6	cratering

are given the values of γd, γnd and their sums for different paints.

γ d: represents the contribution of dispersive forces to γ and γnd represents the contribution of polar forces to γ. γd and γnd can be calculated starting from the experimental values of contact angles of liquids having different dispersive/polar balance dropped on the surface of the coating.

Comparisons between trials C–D and E–F show the results of reducing on cratering. The paints used for trials A and B which exhibit the same surface tension are made of polyesters having significant differences in viscosity (see *Fig. 6*, Polym 1 and Polym 4). The polyester used in trial C has a particular composition, and its surface tension must be dramatically reduced (27 mJ/m2; trial D) in order to get rid of cratering. In these trials the lowering of γ is obtained by addition of the conventional acrylic copolymers. In trial D, a silicone fluid is added to the formulation.

An interesting approach to get a good compromise between storage stability and reduced viscosity has been described by *Eastman* making use of crystalline polyester [23].

4. Degree of Cure

Cure is the term used to describe the film formation process of organic coatings in which relatively low-molecular-weight materials are transformed *via* chemical reactions into a thermoset material.

One major objective of paint manufacturers is to extend the service lifetime of their products. The cross-linking density that can be reached with a thermosetting system is considered, as long as detrimental internal stress does not impart its mechanical properties or reduce its adhesion, as a positive factor favouring the good ageing behaviour of a coating, its resistance to deformation and to chemicals [13].

The network density depends on the polyester functionality and on the extend of the reaction between the epoxy and COOH groups. The increase of cross-linking density can be evaluated among other means by the modification of the gel content of free films, their swelling in DMF and the increase of Tg evaluated by differential scanning calorimetry (DSC).

Table 3

Time [min]	Gel content [%]	Swelling [%]	Tg (DSC)
0	0	soluble	57
5	19	470	63
10	74	200	68
15	80	165	70
20	83	165	70

Table 4. *% of Conversion*

Temperature [°C]	*ASTM* [%]	*Borchardt* [%]	Tg [°C]
160	51	38	78
170	60	54	79.5
180	68	68	82
190	75	77	84.5
200	81	85	85
210	86	90	86

Table 3 shows the evolution for a paint cured at 160°.

After 10 min baking time, it is difficult to evaluate a significant increase of Tg and the build-up of a three dimensional structure is better assessed by the solubility results.

DSC may be used to follow the cure kinetics of an epoxy-polyester powder coating. An exemplary thermogram of a polyester-based powder heated at an uniform speed of 20°/min is shown in *Fig. 10*. The main characteristics of the system may be identified, Tg (56°8), endotherm from the relaxation of the binder (60°5), total heat of the reaction (20.2 J/g), maximum of the exotherm (176°) and outset of the reaction (130°). However, a system which is fast from a kinetics point of view (speed of heat evolution) is not necessarily fast, regarding the formation of a cohesive network. In fact, it is the conversion of the reactive groups that can be correlated to end-use performance property data such as impact resistance.

From the measured exotherm in the thermogram, it is possible to collect valuable information on the addition kinetics. *Borchardt* and *Daniels* make the assumption that the heat evolution is generated by a fully completed reaction, and that the heat generated during any time interval is proportional to the number of molecules having reacted during this time [15].

$$F(\mathrm{t,T}) = \frac{H(\mathrm{t,T})}{Ho}$$

$F(\mathrm{t,T})$ = fractional extent of conversion
$H(\mathrm{t,T})$ = partial heat of reaction involved up to a specific time and temper ature
Ho = total heat of reaction

$$\frac{\mathrm{d}F(\mathrm{t,T})}{dt} = k[1 - F(\mathrm{t,T})]^n$$

n = order rate reaction

taking into account the *Arrhenius* equation $k = A\exp(-E/RT)$ where the change of heat flow with increasing temperature is used to obtain a working expression in terms of measurable experimental parameters [16].

A = *Arrhenius* frequency factor (s^{-1}) and
E = activation energy (KJ/mol)

$$\ln\left[\frac{1}{Ho}\,\frac{\mathrm{d}H(\mathrm{t,T})}{\mathrm{d}t}\right]$$

$$= \ln A\,\frac{E}{RT} + n\ln\left[\frac{Ho - H(\mathrm{t,T})}{Ho}\right]$$

The reaction kinetics parameters n, E, $\ln A$ and, thus, the rate constant k may be obtained simultaneously from this equation using a linear multiple-regression analysis. This allows the prediction of the degree of conversion for specific temperature-time profiles (*Fig. 11*).

Another approach to determine the kinetics parameters is based on the fact that the peak maximum temperature changes with the heating ratet (*Fig. 12*). This

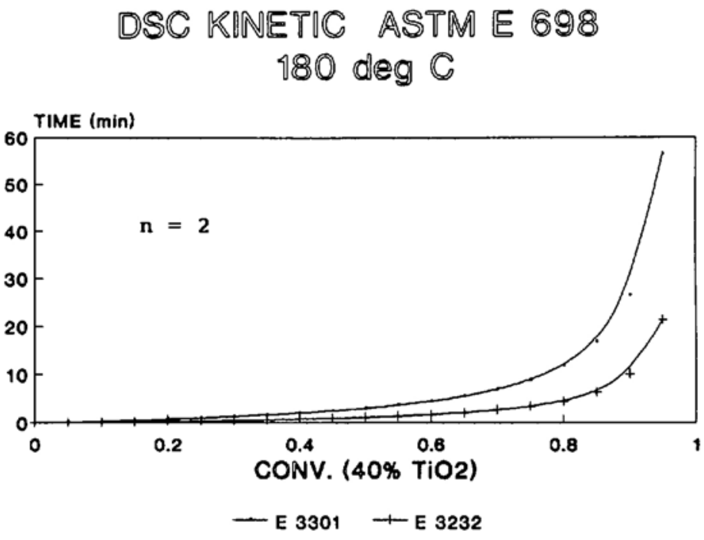


Fig. 15

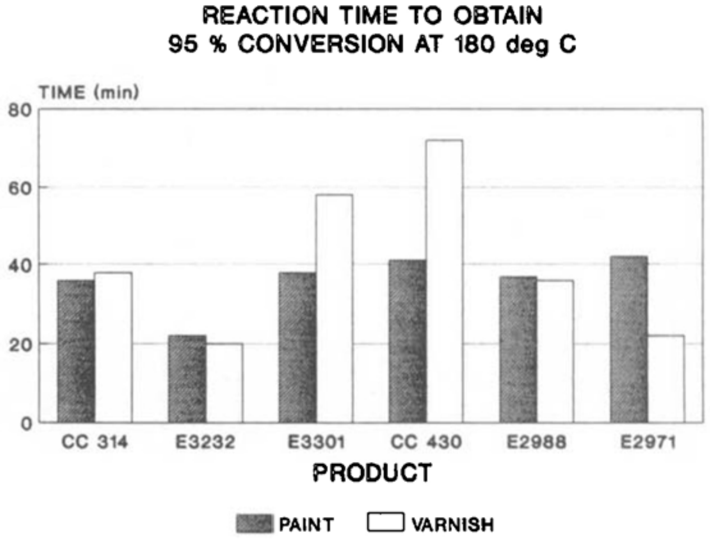
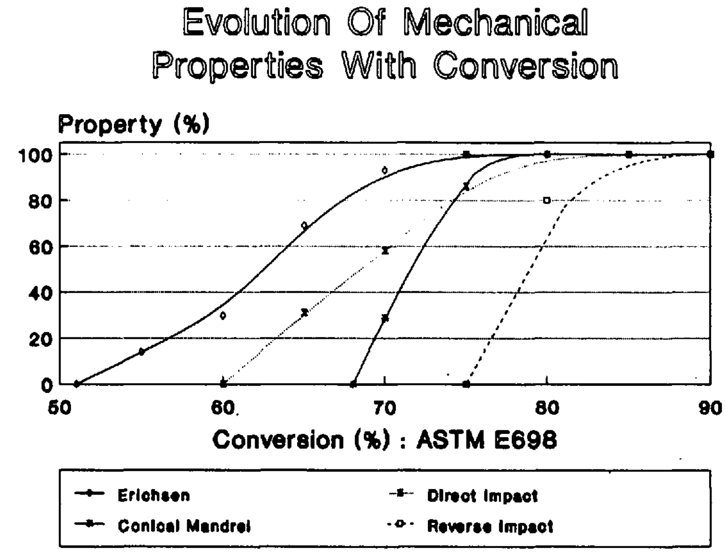
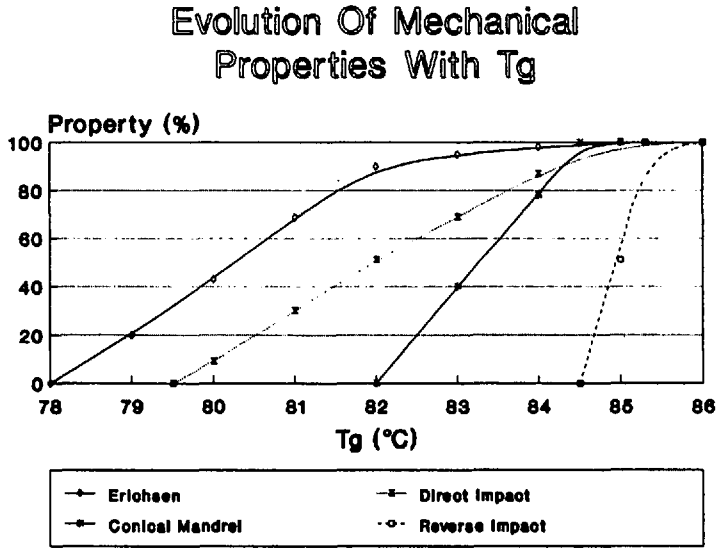


Fig. 16



Conical Mandrel : 3 mm

Fig. 17



Conical Mandrel : 3 mm

Fig. 18

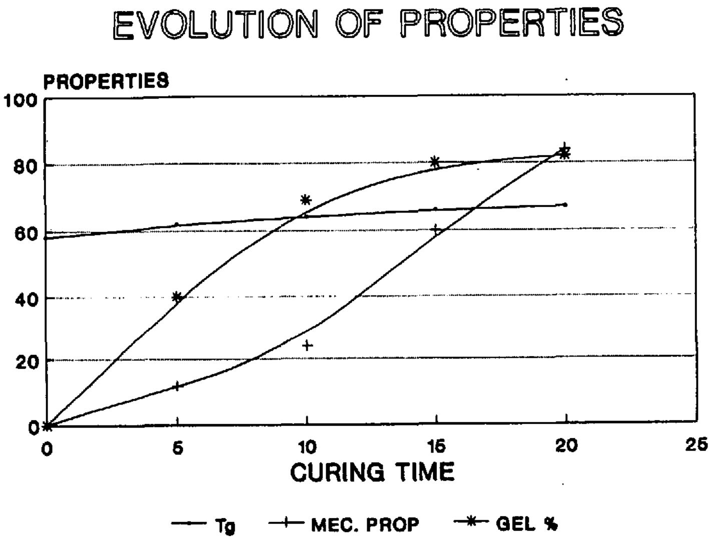


Fig. 19

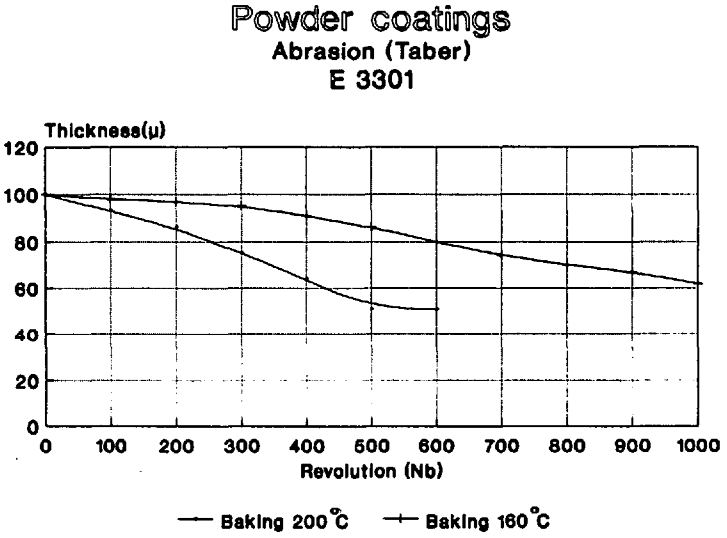


Fig. 20

method developed by *Duswalt* has been adapted as *ASTM E698–79* standard.

The calculation makes three restrictive assumptions:

1) the peak maximum represents a point of constant conversion for each heating rate; *2*) the temperature dependence of the reaction rate constant obeys the *Arrhenius* equation; *3*) the reaction is first order.

From the plot of log B/T^2 (B = heating rate) *vs.* 1/T, the activation energy of the *Arrhenius* equation can be calculated as well as

$$A = B\,E\,e\,\frac{E/RT}{RT^2}$$

If these hypotheses are verified it is possible to calculate the conversion in function of time at different temperatures (*Fig. 13*).

However, this information has to be examined with care. In *Figs. 14* and *15*, we compared starting from the same kinetic parameters the evolution of the conversion at 180° of two paints based on different polyesters considering a first or second reaction order. Depending on the assumption made on the order, large differences are observed, mainly at higher conversion. However, it seems likely that as the reactive components are close to stoichiometry that a second-order reaction will better suit the kinetic reaction between epoxy and carboxylic groups.

In *Table 4*, we compare the % of conversion calculated according to the methods of *Borchardt* or following *ASTM E698–79* ($n = 2$) after 10 min curing at different temperatures.

We observe a large disagreement between the two theories mostly at low conversion. If we compare with the evolution of Tg, the degree of conversion obtained following *ASTM* ($n = 2$) seems more realistic.

If it is difficult to know the true conversion rate of the reaction making use of a DSC equipment, it, however, appears as a powerful tool, if we want to compare different experimental products to well-established ones. *Fig. 16* compares the time requested to achieve 95% of conversion at 180° following *ASTM E698–79* ($n = 2$) for the same formulations based on different polyesters.

It is interesting to look at the evolution of practical important characteristics of the paint like mechanical properties and ageing with the conversion calculated from DSC measurements. Experiments have been conducted on a 93/7 polyester/TGIC formulation. The paints applied on decreased steel (0.5 mm) at a thickness of 65 ± 5 µ. In *Fig. 17*, we represented the evolution of some mechanical properties in function of the conversion as calculated from *ASTM* (see *Table 4*). *Fig. 18* gives the same evolution following the values of measured glass transition temperatures (see *Table 4*).

The speed of acquisition of a typical property follows the sequence: resistance to slow deformation 12 mm/min (*Erichsen*) > resistance to fast deformation applied on the paint (direct impact) > resistance to bending (conical mandrel) > resistance to fast deformation applied on the back of the panel. These results suggest the importance of elasticity and adhesion of the paint performances. It is important to notice that adhesion (cross-cut test) and gloss are obtained readily at low conversion and may not be taken into consideration as a reliable measurement of cross-linking.

Evolution of Tg appears to be an interesting but delicate way to follow the addition process. For this particular system, a calculated conversion following *ASTM*, of more than 85% is requested to reach the maximum level of resistance against deformation. At such high degree of conversion, the Tg begins to flatten out and the limit between acceptable and good mechanical properties is not accurately detected by DSC (*Fig. 19*).

Abrasion resistance is an important characteristic related to paint erosion. The weight loss of TGIC + polyester systems is considered to be 1 µm/year [17]. From *Taber* abrasion tests (2 x H16 mills, 0.5 kg each), the weight loss observed in function of the number of revolutions for the same paint baked at 2 different temperatures normally indicates that the surface hardness depends on the cross-linking density (*Fig. 20*).

However, this property is much more influenced by the chemical structure of the polyester and its ability to fully cross-link with TGIC which behaviour is probably linked to the mobility of the chains and the speed of viscosity build up (*Fig. 21*).

Another interesting result comes out of the Q-panel evaluation. As shown in *Fig. 22*, the gloss retention of a white paint after exposure to UV B 313 nm rays is not dependent on the curing conditions and after 21 days all the coating level off at 40% retention of the initial gloss. These results have been confirmed with other polymeric structures: paints made of polyesters manufactured from other components exhibit the same gloss retention (50%, in this case) after 41 days whatever the curing conditions are (at least between 170 and 210°) (*Fig. 23*).

These results can be attributed to the fact that the Q-panel test is significant for the photodegradability of the polymer which is more dependent on its structure than on the concentration of the end groups [18].

5. Ageing

The obtaining of a high level of mechanical properties is only one of the numerous requirements which are to be fulfilled in order to meet the specifications for paints to be applied to aluminum frames (*Qualicoat* label, *BS 4842*, *GSB*, *JISK 5400*). These tests are intended to predict the long-term behaviour of coatings exposed to outdoor atmosphere and their ability to protect the metal from the corrosion. Among the evaluations to be performed we may point out *Q UV* exposure, *Sun* test,

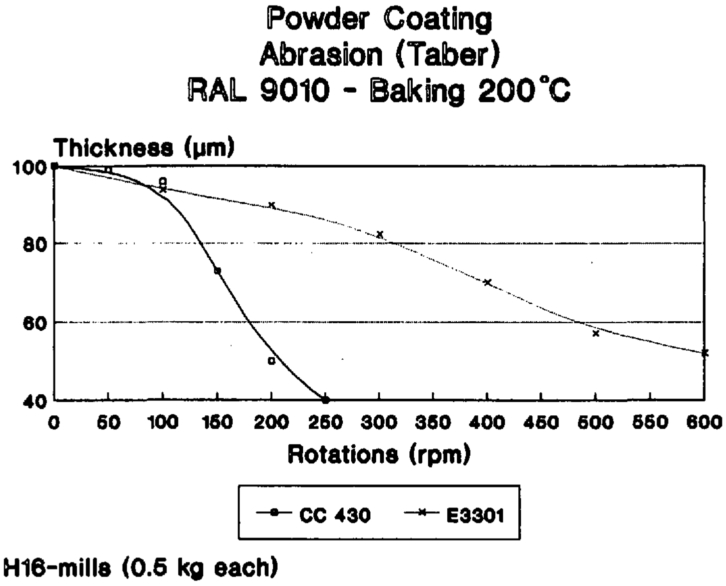


Fig. 21

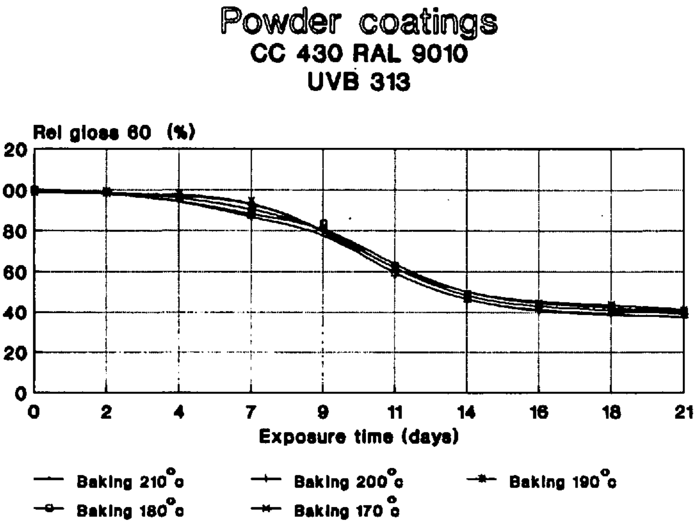


Fig. 22

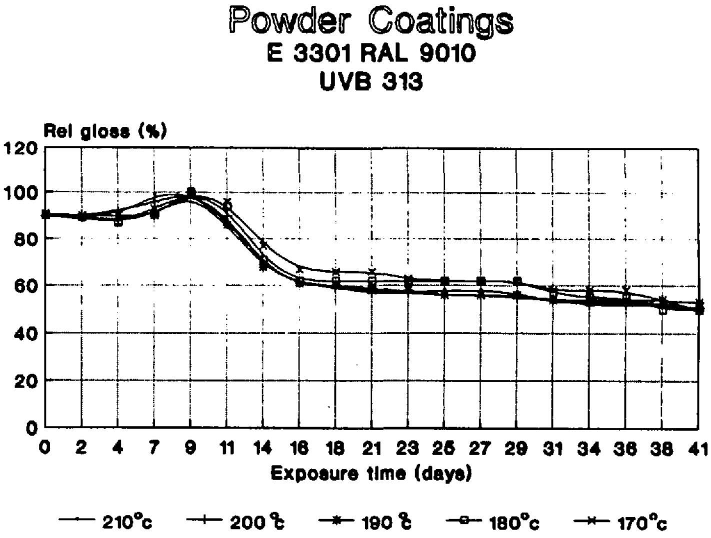


Fig. 23

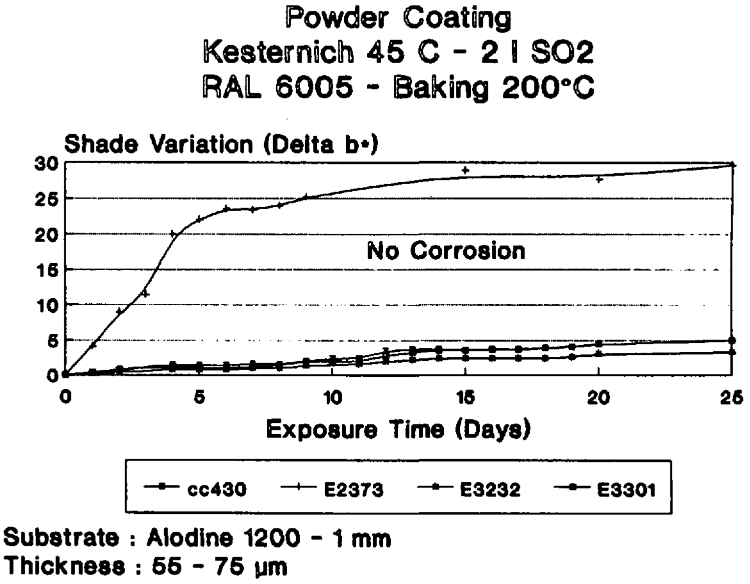
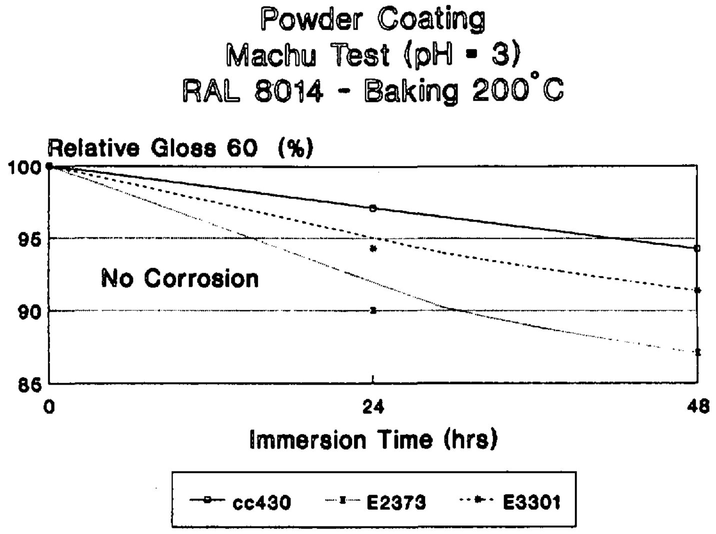
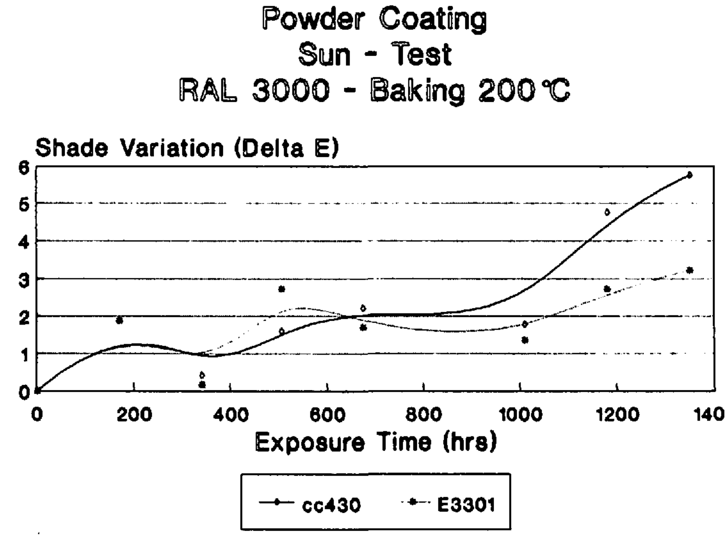


Fig. 24



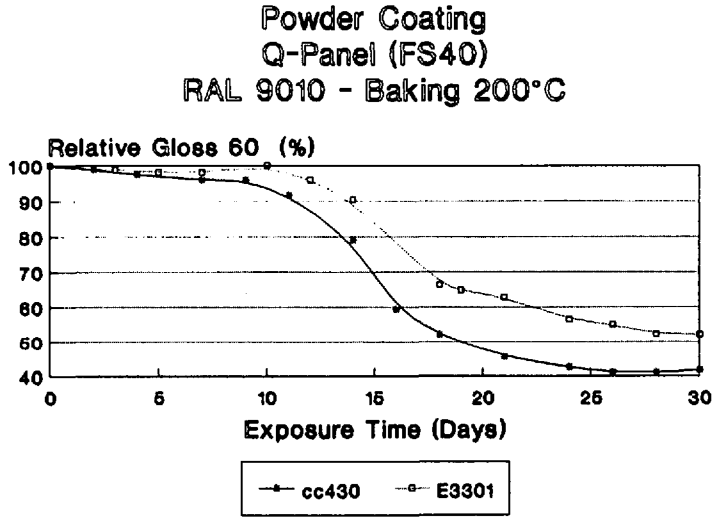
Substrate : Alodine 1200 - 1 mm
Thickness : 55 - 75 µm

Fig. 25



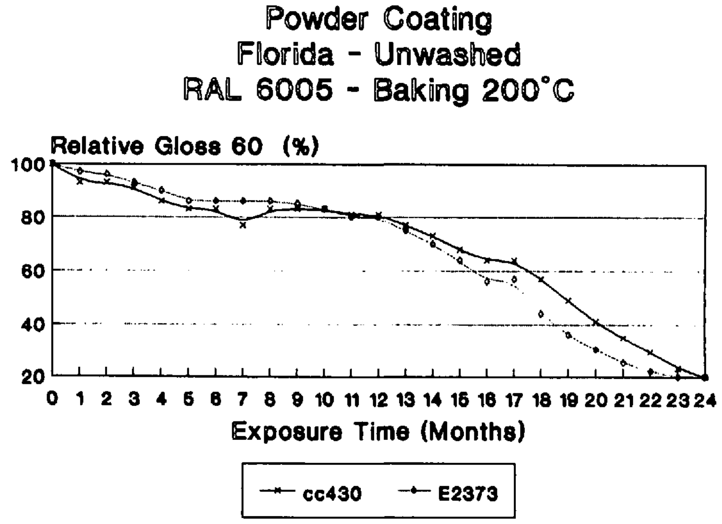
Substrate : Alodine 1200 - 1 mm
Thickness : 55 - 75 µm

Fig. 26



Substrate : Alodine 1200 - 1 mm
Thickness : 55 - 75 µm

Fig. 27



Substrate : Alodine 1200 - 1 mm
Thickness : 55 - 75 µm

Fig. 28

Kesternich, *Machu* test, *Florida* exposure, solvent-, hot-, acetic and alcali-, soft spray-, stain resistances. Results of some typical trials are given in *Figs. 24–29* in various shades (*RAL 8014* = dark brown, *RAL 9010* = white, *RAL 3000* = red, *RAL 6005* = green). Polyesters with the same acid value belonging to old (*CC 430*, TG = 74°; *E 2373*, Tg = 52°) and new (*E 3301*, Tg = 55.5°) generations are compared.

The low Tg of *E 2373* is obtained through plastification with aliphatic difunctional –OH and –COOH compounds. *E 2988* is a carboxylated polyester developed to be used as a clear varnish on top of metallized paint. *Kesternich* and *Machu* tests indicate that it is not advisable to reach a good flow through conventional plastification, because it builds easily hydrolysable ester groups in the polymeric backbone (*Figs. 24* and *25*).

Sun test and Q-panel results indicate that a high Tg has no favourable influence on the accelerated weathering (*Figs. 26* and *27*).

In these tests, the temperature does not exceed 60°. In the *Florida*-exposure test, there is no significant difference in behaviour during the first year, but afterwards the gloss retention remains better for the product with higher Tg (*Fig. 28*). It appears that the increase in free volume and in freedom of movement of parts of molecules of low Tg can result in an increase in permeability for H_2O which will induce the hydrolysis of the polyester. This behaviour is only noticeable after some time (one year in Florida) which may indicate that the phenomenon is autocatalyzed by the appearance of COOH groups when their concentration reaches a critical level.

It is important to note the influence of the pigmentation on the colour stability (*Figs. 28* and *29*).

As far as salt spray tests are concerned, we found that the pretreatment of the metal is certainly the determinant factor affecting the corrosion resistance, when the paint is fully cured. Undercured films are more easily degraded, probably following an acid autocatalyzed mechanism, which induces brittleness and loss of adhesion.

Acidic and salt spray resistances (*E 3301*): *Curing 10 min at 200°*:
1250 h on *Granodine 124*: no rust creeping from the cross; 1250 h on *Alodine 1200*: no rust creeping from the cross < 250 h on degreased steel: 3-mm rust creeping from the cross

Curing 10 min at 190°:
500 h on *Granodine 124*: 3-mm rust creeping from the cross

Curing 10 min at 180°:
< 250 h on *Granodine 124*: 3-mm rust creeping from the cross.

6. Applications

6.1. Precoated Metal

An interesting application of the carboxylic polyester-TGIC application recently introduced in Europe and initially

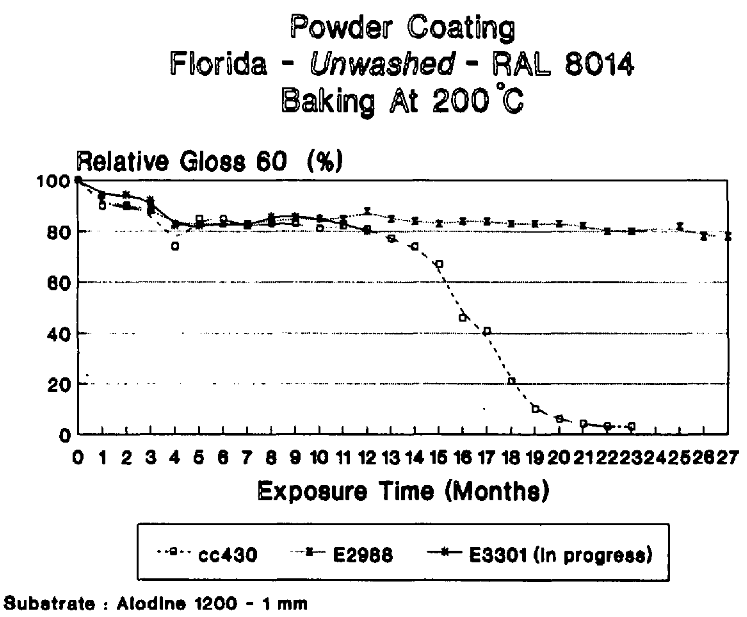


Fig. 29

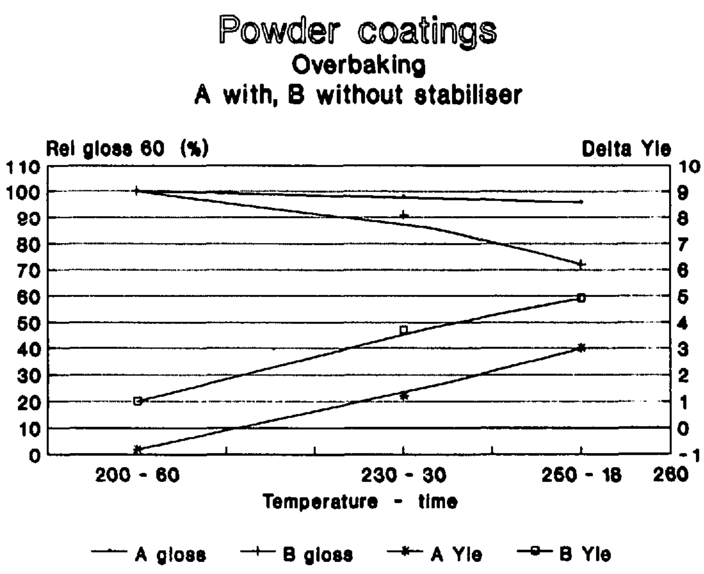


Fig. 30

developed by *Nippon Paint* making use of polyurethane systems is the painting on cut, pretreated steel panels running at about 6 m/min (Pre Coated Metal) [19]. The curing is obtained in a short time (less than 1 min) by heating the substrate with IR radiations at high temperature (250°). In radiation curing, there is a risk of heating the powder before the metal, this results in poor adhesion. The temperature of the IR heating elements must be selected in order to emit wavelengths outside the spectral absorption of the polyester (2.5–3.5 µ). Final baking occurs in a convection oven during 1 min at 230°. The coated metal sheets are embossed at the end of the line. The finished panels are used to manufacture domestic appliances such as refrigerators, washing machines, and microwave ovens (20). The major requirements such a paint has to possess are high gloss, very good flow, flexibility (O–*T* bending at 20°) and resistance to detergent and stain resistance from various chemicals.

Due to the particular application conditions and required characteristics of the paint, the structure of the polyester has to be specially designed, and the paint has to be formulated with additives such as flowing aid, anti-crater agent, in order to obtain very low surface tension (*Table 2*, Trial D) addition catalyst and anti-oxidant to improve the high temperature resistance (*Fig. 30*).

The advantages of the PCM technique compared to the painting of shaped appliance goods are: reduction of inventory, minimization of labour costs, in plant coating and quality control, low reject rate, better edge coverage, and higher chemical and physical properties. Frequently, in powder coating one property may be detrimental to another. In PCM polyester, the high resistance against staining which requires high cohesive energy density in the order of 640.000 J/mol and a certain level of crystallinity is obtained by chemical components which are not suitable for UV resistance (*Fig. 31*).

6.2. Tribo Ionization

Eltrostatic powder coatings have, in recent years, been applied by means of guns that charge the particles through the *Corona* principle. In this equipment, a high voltage (30–100 keV) is applied to, at least one electrode, located into the sprayer which is sparged with flowing ionized air. When the air molecules collide with a powder particle, a transfer of electrical charge occurs, and the solid particle will follow the field lines towards the earthed metallic object to paint.

Due to the electrostatic field, many problems are encountered by the screening effect of the *Faraday* cages hindering the penetration of the paint in geometrically complicated areas. To overcome this difficulty, tribo charging of powders has been developed. The tribo effect is based on the fact that, when two materials having dissimilar dielectric properties brought into contact and then separated, results in a charge transfer from one material to the other [21]. Technically, the powder particles (ground to 40 to 50 µm) are suspended by air in a fluidised bed and transfer under pressure in the gun. The driving force for charge exchange is related to the difference in the work function of the contacting surfaces that can be evaluated by *Kelvin*-type contact potential difference measurements.

In this technique, the electrical charges are localized on the paint particles, and there is no ionization of the air located between the gun and the substrate. The resulting sharp decrease of the electrical field allows a better coverage of the intricate shaped articles as well as a far better wrapping effect.

The absence of back ionization also allows to get a smoother surface appearance and less porosity of the film.

For mechanical (abrasion resistance) as well as for physical reasons (electronegativity of fluor), the PTFE (*Teflon*) is used

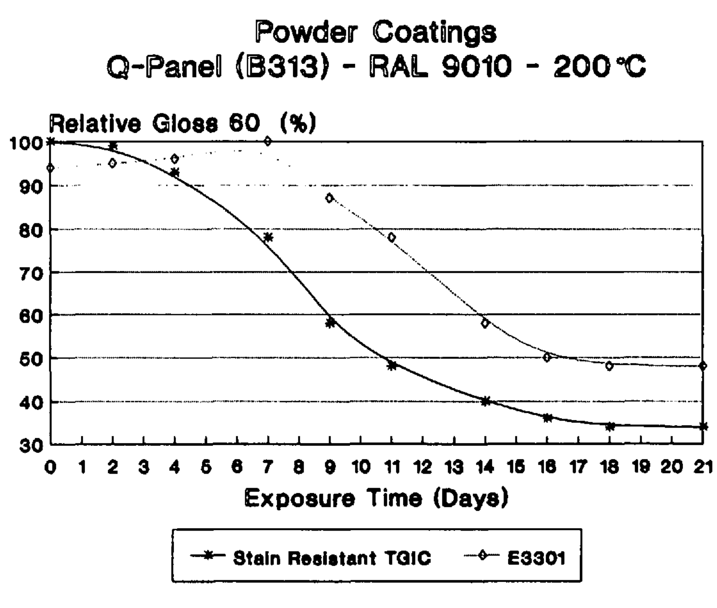


Fig. 31

in tribo guns as the friction material. The dielectric constant of PTFE being very low ($\varepsilon = 2.1$), all substances with higher will get a positive charge when brought into intimate contact and separated from PTFE. Compared to other system used in powder coating such as epoxies + dicyandiamide ($\varepsilon = 4$), polyesters + blocked isocyanates ($\varepsilon = 5$), or certain hybrid systems ($\varepsilon = 4$), the mixtures polyesters + TGIC have not been found to be appropriate ($\varepsilon = 3$) for charge acceptance due to small differences in dielectric constant with *Teflon* [22].

By analogy with what is used in xerographic toners, the addition of quaternary ammonium of phosphonium salts has been found to increase the positive charging characteristics of the powder, improving the transfer efficiency. Addition of colloidal oxides like SiO_2 or Al_2O_3 due to their specific surface have also been used to improve the charging characteristics. The use of external additives, however, brings the drawbacks associated with a non-uniform composition leading to problems associated with segregation and difficulty of paint recycling. To overcome these drawbacks, work is now in progress to introduce functional groups in polyesters to determine and control their triboelectric properties.

7. Conclusions

In this communication, we have discussed some aspects of the powder coating system based on polyester-TGIC mixtures:

- the TGIC isomeric composition
- the main parameters affecting their surface appearance
- the influence of extend of reaction on coating properties
- their ageing behaviour
- development in PCM and tribo applications

Apart from these selected topics, there are many other basic items or new application fields of polyester based powder coatings which would be interesting to examine such as the painting of non-metallic substrates, alternative cross-linkers to TGIC, new paint manufacturing process, low bake temperature systems, dry clear coat on dry paint, *etc.*

All these developments contribute to the growth of the sole high performance, air-, water- or soil-non-polluting coating technique.

I would like to thank my colleagues of the *Polycondensation Group*; *D. Maetens*, *W. Demarteau*, *M. Baudour*, *L. Moens*, *J.-M. Hoebeke*, and *N. Dewez* for their help in this work.

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Fortsetzung und Schluss im nächsten Heft.

Chimia 44 (1990) 336–338
© Schweiz. Chemiker-Verband; ISSN 0009–4293

Enantiomers of 2,2′-Spirobichromenes**: Energy Barrier for Thermal Racemization during HPLC on Tribenzoylcellulose

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Abstract. As a first case in the field of spirochromenes, the energy barrier for thermally reversible ring opening of 2,2′-spirobichromenes (*Scheme*) is measured by racemization of preparatively enriched enantiomers. In addition, this barrier is estimated *via* racemization *during HPLC* (*Fig.*) on tribenzoylcellulose without preparative enrichment. The significance of the latter procedure is discussed.

Introduction

Spirochromenes have been studied very actively in the past, since many of them are photochromic owing to a C(sp^3)–O bond opening reaction [2]. The thermal behaviour of these compounds has received less attention, probably because thermochromism has been encountered less frequently and was considered to be less spectacular. The only barriers for reversible ring opening have been reported for some spiro[chromene-2,2′-indolines] [3] and spiro[chromene-2,1′-(2)-oxaindans] [4]. In both cases, diastereotopic groups were a prerequisite for variable-temperature ^{1}H-NMR measurements. However, this would not be necessary if separated enantiomers were available to be racemized, in order to determine their barriers for ring opening. For instance, 2,2′-spirobichromenes (*Scheme*) might be studied in this way. Indeed, *Okamoto et al.* [5] resolved some bridged diaza derivatives of this series by HPLC on (+)-poly(tritylmethacrylate)/SiO_2. However, they did not detect thermal racemizations [5]. Therefore, we intended to separate the enantiomers of simpler 2,2′-spirobichromenes (*Scheme*) and to determine their barriers for ring opening.

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** Chiral 2*H*-Pyrans, Part 2; Part 1: [1].