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THERMOSETTING EPOXY RESINS FOR LACQUER PRODUCTS WITH HIGH SOLID--ETC(U)
JAN 80 T AUDYKOWSKI, R SCHMID

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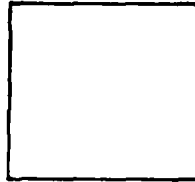
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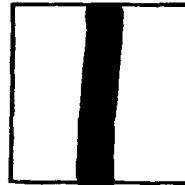
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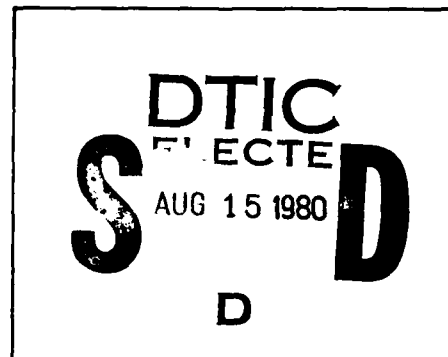
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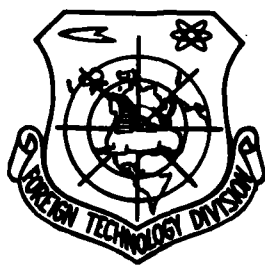
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THERMOSETTING EPOXY RESINS FOR LACQUER PRODUCTS
WITH HIGH SOLIDS CONTENT

by

T. Audykowski, R. Schmid



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THERMOSETTING EPOXY RESINS FOR LACQUER PRODUCTS

WITH HIGH SOLIDS CONTENT

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1. Introduction

165

Legal restrictions connected with the protection of environment and increasing difficulties with the energy have presented new problems for the paints and lacquers industry. These two factors will exert, no doubt, also a large influence upon the development of new techniques in the production of coating materials. New methods of depositing lacquer products, for instance the powder spraying or electrophoresis, cannot satisfy all the requirements of industrial consumers. This fact was clearly established in many publications and in many discussions. In effect, the need arose to develop yet other types of lacquers which would not contain much of harmful substances and would not contaminate the environment.

Among new solutions, good prospects of development are anticipated for products with a high solids content, the so-called "high solids". A number of factors contribute to an increasing interest in this type of lacquer products. The basic "high solids" can be developed utilizing the known raw materials and without the necessity of incurring high expenses for the research studies. These products can be deposited by means of existing application facilities avoiding thus the need for unpopular new investments. Because of

reduced emission of solvents, the "high solids" products possess real ecological advantages. At the same time they enable to obtain thicker coatings, hence an intensification of production.

A number of recent publications /1-9/ contain a review of the state of art of the technology of "high solids" products and describe various aspects and problems of their application. The majority of newly used adhesives are based on combinations of polyester or acrylic resins with functional hydroxyl groups - with amine resins. Lately, an increasing interest has also been shown in two-component "high solids" products, based on new polyurethane compositions and intended for application in the auto industry /10/. In addition to their high resistance to atmospheric conditions, the products of this type enable also to make real savings in the consumption of energy since they crosslink at low temperatures. This is of high importance since, in addition to the protection of environment, it is very desirable to reduce the consumption of energy when crosslinking the coatings.

The "high solids" products based on epoxy resins are still in the developmental stage (2, 9). Although the epoxy systems are generally characterized by the large variability of the resin/hardener combinations and offer larger possibilities than the other groups of polymers, the introduction of "high solids" products to practical applications has been delayed by certain side factors. Experiments have shown that one of the main obstacles to broader application of these products is a high reactivity of components,

requiring the necessity of use of facilities for spraying two-component systems. This article will describe two selected new "high solids" products formulated on epoxy base. Results of our investigations indicate the possibility of application of these systems in the formulation of compositions for the base and interlayer coatings in the auto industry, and for deposition by the coil-coating method.

2. New epoxy products of "high solids" type

The systems described here have been chosen as a result of many tries, which took also into consideration the requirements of the protection of environment and saving of energy. General properties of these systems, as well as those of the resins and hardeners used, are presented in Table 1.

Composition: epoxy resin/ acid dianhydride

Epoxy resins crosslinked with various monoanhydrides play an important role in applications for electrotechnical industry /11, 17/. However, the long time required for hardening, losses resulting through evaporation and mediocre properties of coatings prevented their use in the area of protective coatings.

As a result of broad research work carried out in the last years a new dianhydride, based on modified trimellitic anhydride (Table 1), can be recommended as a hardener for coatings. This compound easily dissolves in cheap organic solvents, and mixes

well with various resins used in the technology of protective coatings. It shows also a high reactivity in relation to epoxy oligomers of different chemical structure /12/ (Table 3), whereas the obtained coatings possess good general characteristics. When this hardener is applied in combination with certain selected cycloaliphatic or heterocyclic epoxy resins based on 5,5-dimethylhydantoin, one obtains resins with high resistance to the action of atmospheric conditions /12/. The mechanism of hardening of epoxy resins with acid anhydrides was explained in 1956 /13/.

All the reaction steps following each other in the process of crosslinking, i.e., formation of monoesters, diesters and esterification, occur as a result of the simple mechanism of addition. For this reason no side products are formed during the reaction. And just because of this feature the hardening with anhydrides is advantageous in application to protective coatings, since in this area one can anticipate stricter and stricter legal requirements relative to the reduction of the emission of contaminants.

The composition "high solids" 1821/XB 288, proposed by us, fulfills these requirements. When the coating is heat-set under the recommended conditions, it is only the solvent that evaporizes but there is no loss of coat-forming components (the coefficient of by-products is 0 %). All other "high solids" systems in which crosslinking occurs as a result of the reaction of polycondensation, i.e. combination of polyester or acrylic resins

with amine resins, lose more or less of volatile components arising from the coat-forming substances during the process of heating. The losses amount to 5-20 %, depending on the initial materials. These volatile components may be sometimes more toxic than the solvents, and they may cause real problems in the drying booth during heat setting and increase the costs of obtaining the coating. In cases where the protection of environment is very important, it is always necessary to evaluate critically the composition of volatile byproducts. The obtained value of 0 % for byproducts coefficient during the crosslinking of our system is rather unexpected, since the resin used is a mixture of low-viscosity epoxy oligomers. Such selection of resin was dictated by assumption of obtaining the product with a high content of nonvolatile substances at viscosities suitable for use.

High reactivity of the components of resin with the XB 2883 dianhydride, enhanced through such accelerators as dimethyleneglycol sulfide or tin octoate, plays a positive role in prevention of the volatilization of epoxy oligomers. A high reactivity in situ on the base is necessary to obtain well crosslinked network of the polymer, ensuring good properties of the coat. Results of investigation of chemical and mechanical properties of the coatings obtained from the compositions proposed by us are presented in Table 2.

These results indicate that the system crosslinked with dianhydride with the addition of 1-2% dimethyleneglycol sulfide

as an accelerator, even at low temperatures of heat setting provides coatings with very good mechanical properties and also good chemical resistance. Tin octoate proves to be an even better accelerator (Table 3).

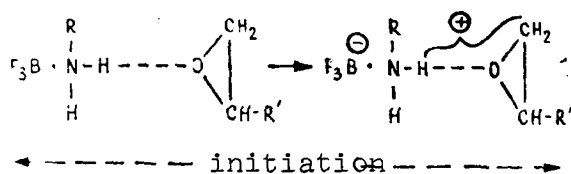
Good properties of coatings enable us to recommend the application of these products for internal and external coating of metal containers, for coil coating, and for other industrial uses. A shortcoming of this system, i.e. limited time of the suitability for use (1-7 days), can be easily circumvented, if it is necessary, by the use of suitable dosing pumps and by supplying premixed product to rollers or spray guns.

Composition: epoxy resin / BF_3 complex - amine

Since the proposed-by-us "high solids" system consisting of epoxy resin hardened with XB 2883 dianhydride has a limited shelf life, we began studies to develop slower reacting compositions, based on BF_3 -amine complexes. Similarly to the case of anhydrides, the BF_3 -amine complexes have also found only a limited application in the field of protective coatings. On the whole, they are used as slowly-reacting hardeners for gluing of mica in the production of laminates /14/.

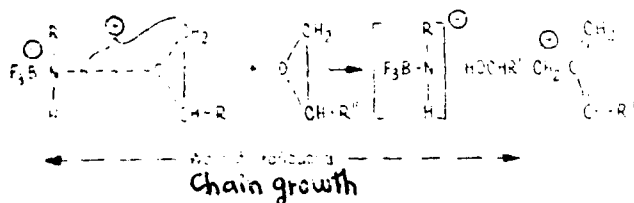
The mechanism of crosslinking with BF_3 -amine complexes was the subject of more studies and discussions than in the case of other hardeners. At present, it is considered that the dissociation theory is obsolete. More recently postulated view is that BF_3 -amine

are polymerization catalysts and act as Brönsted acids /15/. In the initial phase a weak bond is formed between hydrogen of the amine and oxygen of the epoxy group with a partial positive charge at the oxygen of the epoxy group.



The chain grows as below, and as the temperature increases a point is reached at which this chain growth reaction will be sufficiently fast to effect crosslinking of the coating.

198



In our investigations we used a new liquid compound based on a complex of a heterocyclic amine with BF_3 and designated as 1772. This compound is interesting as a hardener for the products of "high solids" type intended for various applications.

We examined 14 liquid epoxy resins and low-viscosity oligomers, and we selected the CY 182 resin as the most suitable one. It follows from Table 2 that mechanical properties of coatings

from the CY 182/1772 composition are comparable to those of the composition crosslinked with dianhydride, except for the resistance to the action of acids, which is lower. The advantages of the CY 182/1772 composition are: a higher content of nonvolatile substances and a higher period of suitability for use (shelf life). Properties of these coatings indicate that this system may be applied for coating of containers, for applications by the coil-coating method, and for base and interlayer coats.

Thermoanalytical studies

Thermoanalytical studies enable to obtain valuable information pertaining to the mechanism of crosslinking of coatings, their thermal resistance, thermal durability (glass temperature T_g), and decomposition of the polymer. We examined all the compositions (Table 3) by the method of thermogravimetric analysis (TGA), rate of vaporization (DTG), differential thermal analysis (DTA), thermomechanical analysis (TMS), and torsional oscillation analysis (TSA).

The course of hardening of coatings is characterized by two processes: vaporization of the solvent and a reaction which leads to crosslinking. Depending on the type of solvent and the mechanism of crosslinking these two processes may superimpose on each other. In this case, estimation of TGA results is unreal. However, simultaneous recording of the weight change (TGA), rate of vaporization (DTG) and differential thermal analysis (DTA)

enables an independent clarification of both processes.

Figure 1 presents combined results of thermal analyses of Composition I without an accelerator (rate of heating $\beta = 4^{\circ}/\text{min}$). The first DTG peak (93°C) corresponds to evaporation of the solvent. As the temperature increases, the sample undergoes hardening without any weight change. One more exothermic peak (132°C) occurs when we change to DTA. This temperature, at which the reaction proceeds at the highest rate, is taken as a measure of the reactivity of the composition. When the temperature is increased further, the sample begins to decompose, which is denoted by a distinct peak (370°C) of the DTG analysis. On further increase of the temperature (488°C) the tar remaining after the pyrolysis of sample begins to be oxidized. The temperature of decomposition reflects the thermal stability of the polymer, whereas the amount of tar residue is connected with resistance to creeping currents, important in electrical applications (Figure 1).

An addition of accelerator increases distinctly reactivity of the composition. The addition of accelerator A (diethyleneglycol sulfide) gives in effect the DTA peak at a temperature about 50°C lower than in the case of the composition without accelerator (Table 3). The vaporization peak is lowered by about 30°C . A part of solvent becomes "squeezed out" during the reaction of cross-linking, and the remaining part is retained in the crosslinked system. In effect, coatings with an added accelerator contain small amounts of volatile substances.

The accelerator B (tin octoate) enhances the reactivity of composition even more than does the accelerator A.

In composition II, after evaporation of solvent the catalytic hardening proceeds in two stages. Here also the more reactive composition II C is characterized by a smaller content of volatile substances. This is an important advantage of our new "high solids" systems. Other products of this type - products based on polyester resins crosslinked with hexamethoxymethylomelamine and conventional epoxy-urea-formaldehyde systems (III and IV) - contain 23% and 60% of volatile substances, correspondingly. The activation energy of vaporization E_{Ae} and of reaction E_{AC} have been defined by J.H. Fynn and L.A. Wall /16/ as:

$$E = -4,35 \frac{d \log \beta}{d \left(\frac{1}{T_{max}} \right)} \ln \left[\frac{\text{cal}}{\text{mol}} \right]$$

where β = rate of heating.

As an example, Figure 2 shows the activation graph with coordinates of the rate of heating and the temperature of maximal vaporization or the temperature of maximal reactivity, for composition I. The results are entered in Table 3.

Large activation energies are typical for systems hardened catalytically without accelerators. Rather large activation energies are also obtained for composition I hardened with dianhydride and accelerator B. Such systems crosslink fast at high temperatures

and slowly at lower temperatures. This fact provides, in effect, products with relatively long period of suitability for use (shelf life, pot life). It follows also from Figure 2 that "vaporization" and "crosslinking" are separate processes for composition I (continuous lines) in the whole range of temperatures, whereas the addition of accelerator B moves these processes closer to each other (interrupted lines). 69

Table 5 shows that both compositions I and II possess high decomposition temperatures. Thus our new compositions have better thermal stabilities than the "high solids" systems on the basis of polyester resin (6MMM) and conventional epoxy-urea systems, i.e. compositions III and IV. As follows from Table 5, changes in conditions of crosslinking have no effect on thermal resistance.

Table 6 shows the glass temperatures, T_g . For compositions I and II they lie around 80-100°C. Crosslinking at 220°C raises T_g by 15-20°C. The addition of accelerator A reduces T_g considerably, presumably because of its plasticizing effect and/or destabilizing effect by the retained solvents. On the other hand, the composition of high reactivity (with accelerator B) shows a small increase of T_g (7°C).

Evaluation of suitability of the new lacquer materials for coating the automobiles and for deposition by the coil-coating method

The automobile industry has often been the initiator in development of new concepts and the driving force for their realization.

At present, the auto industry in many countries is interested in the introduction of new coat-forming materials, not contaminating the atmosphere and containing but little of harmful substances. The energy saving acquires also a larger and larger importance.

Earlier investigations indicated that our new adhesives could be useful for applications in the auto industry. Hence we examined these products in the base paints. Zinc chromate was used as anticorrosion pigment. Table 7 shows properties of liquid bases and of the coatings from them. The obtained results indicate that mechanical properties of coatings from our new epoxy adhesives are higher than the properties of standard materials. The contents of nonvolatile substances in the material for application is 75-78 %, enabling to reduce considerably the emission of solvent. No byproducts of reaction are evolved during the crosslinking of composition I. The system crosslinked with dianhydride XB 2883 enables also to save energy, since it can be hardened in the time of 10 - 20 minutes at the temperature of 90°C, without worsening the mechanical and anticorrosion properties of the coating.

Both compositions deposited on bonderized steel give excellent protection after 240-hours action of saline chamber. Nearly the same good results are obtainable on steel plates. After 500 hours' stay in humidity chamber, simulating tropical conditions, only small bubbles appear on the base from nonbonderized steel. Good adhesion properties and resistance to rusting and blistering were obtained also in testing of coatings after immersion in water, although the

coating crosslinked with BF_3 gives a somewhat poorer performance.

The second stage of our examination comprised checking the suitability of these products to deposition on alodized aluminum plates by the coil-coating method. Very good results were obtained (Table 8), particularly a large resistance to deformations (T-Bend 2), very good adhesion, resistance to the action of MEK and corrosion, confirming the high quality of new products.

In general, it can be stated that the two new epoxy compositions are suitable for obtaining the base and interlayer coatings for the auto industry, and for deposition by the method of coil-coating. Their main advantage is a smaller content of solvent and of volatile byproducts. The epoxy composition crosslinked with dianhydride enables also to attain a considerable saving of energy necessary for crosslinking.

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REFERENCES

1. Mercurio A., Lewis S. N.: *Journal of Paint Technology*, 47, No 667, 37, (1975)
2. Young R. G., Howell W. R., Jr., *Modern Paint and Coatings*, March 1975, 43.
3. Lunde D. I., Wetzel L. A., Freund W. J.: *Modern Paint and Coatings*, March 1975, 23
4. Yonek Kenneth P., Fox G. L., Hudson G. A., White R. L.: *Modern Paint and Coatings*, March 1975, 53
5. Larson J. M., Tweet D. E.: *Modern Paint and Coatings*, March 1975, 31
6. Gott L.: *Journal of Coatings Technology*, vol. 48, No 618, July 1976, 52
7. Gibson D. V., Leary B.: *Journal of Coatings Technology*, vol. 49, No 625, February 1977, 53
8. Stoye D., Andrejewski W., Dörffel J.: *Fatipac-Congress book*, 1976, 665
9. Vettors Ch. M.: *Modern Paint and Coatings*, March 1976, 55
10. Uerdingen W., Findeisen K., Wagner K.: *Fatipac-Congress book*, 1976, 615
11. Lee H., Neville K.: *Handbook of Epoxy Resins*, 1967
12. Audykowski T., Knecht E., Habermeler J.: *Fatipac-Congress book* 1974, 100
13. Fisch, Hofmann, Koskikallio J.: *Appl. Chem.* Oct. 1966
14. Lee H., Neville K.: *Handbook of Epoxy Resins*, 8-13, 8-10, 11-2.
15. Harris J. J., Tamin S. C.: *J. Appl. Polym. Sci.*, 10, 323, 1966
16. Flynn J. H., Wall L. A.: *Polym. Lett.* 4, (1966), 223
17. Stierli R.: *ETZ-B*, 1966, 20, 649-654

Table 1. General properties of new epoxy compositions of "high solids" type

1 Rodzaj żywicy i utwardzacza	2 Żywica 1821	3 Utwardzacz XB 2883	4 Żywica CY 182	5 Utwardzacz 1772
6 Skład chemiczny:	7 modyfikowany, alifatyczny ester glicydylowy	8 modyfikowany bezwodnik trójmelitowy	9 dwuglicydylowy ester kwasu czterohydroftalowego	10 kompleks BF ₃ (amina heterocykliczna)
11 Właściwości:				
12 Lepkość, 25°C, m Pas	180	1600—2500	450—550	15 000
13 Zawartość substancji nielotnych, %	100	70 ± 2	100	100
14 Kolor (Gardner)	10	6—7	2—3	16—17
15 Liczba epoksydowa rów/kg	5,9	—	6,3	—
16 Ciężar równoważnikowy	170	358 (250)	159	—
17 Udział wagowy w mieszaninie	100	104	100	4
18 Zawartość substancji nielotnych przy stosowaniu	75—80%		78—91%	
19 Przydatność do stosowania (dni)	21—7		60—120	
20 Polecane warunki wypalania	20 min. w 90—140°C lub 2 min. 250°C		20 min. 170°C lub 2 min. 250°C	
21 Współczynnik produktów ubocznych, %	24 0		24 3—6	
22 Polecane zastosowanie	24 grunty i międzywarstwy przemysłowe i samochodowe, coil coating, malowanie opakowań		24 grunty i międzywarstwy przemysłowe i samochodowe, coil coating, malowanie opakowań	

Key: 1 - Type of resin and hardener; 2 - Resin 1821; 3 - Hardener XB 2883; 4 - Resin CY 182; 5 - Hardener 1772; 6 - Chemical composition; 7 - Modified Aliphatic glycidyl ester; 8 - Modified Trimellitic Anhydride; 9 - Diglycidyl ester of tetrahydrophthalic acid; 10 - BF₃ complex (heterocyclicamine); 11 - Property; 12 - Viscosity, 25°C, m Pas; 13 - Content of nonvolatiles, %; 14 - Color (Gardner); 15 - Epoxy number, row/kh; 16 - Equivalent weight; 17 - Weight part in mixture; 18 - Content of nonvolatiles at application Pot life (days); 19 - Recommended heating conditions; 20 - By-products coefficient, %; 21 - Recommended application; 22 - at; 23 - or; 24 - Base and interlayer coatings, industrial and automobile, coil coating, painting of containers

Table 2

Properties of new epoxy compositions of "high solids" type
and properties of their coatings
(coatings of thickness 10 μ m - in nondried state - deposited with
an applicator on clean aluminum tapes of thickness 0.3 mm)

Hardened with	Dianhydride XB 2883	Amine complex ZBF ₃ 1772
Composition of tested product	Resin 1821 100 Butyl octane 17 FC430(10%) 0.5 Catalyst 1354 3.4 HB 2883 104	Resin CY182 100 Butyl octane 10 Si840(60%) 0.5 Hardener 1772 4
1	2	3

Properties

Content of solids at application, %	78,5 30 min./120°C	91 10 min./200°C
Conditions of crosslinking		
Initial viscosity at 25°C	111 m Pas	175 m Pas
Viscosity after	6 hours: 395 mPas	8 weeks 36 mPas
Byproducts coefficient, %	0	3,2
Spreading/wetting	very good	very good
Color of coating	clear, colorless	clear
Mechanical durability	very good	very good
Adhesiveness, net 1 mm according DIN 53 151	Gt-0	Gt-0
Bending (1 mm 180°)	sustains	sustains at TFS
Impact direct/reverse (cm.kg)	160/160	180/180
Resistance to acetone	sustains 20 passes	2 hours
Resistance to sterilization (1 hour/120°)	sustains	sustains at TP and TFS
Resistance to 2% acetic acid (6 hours/96°)	sustains	breaks down
Resistance to 5% H ₃ PO ₄	4 weeks at 25°C	7 days
T-Bend (on 0.7 mm alodized aluminum plates	1 T po 2 min.) 1 T po 2 min. 250°C	1 T (3 min./250°C) 1 T (3 min. /250°C)

Table 3. Results of the crosslinking of various coating compositions (rate of heating = 4°C/min)

1 Zestaw powłokowy		2 TG → odparowanie		3 DTA → sieciowanie		4 TGA		
		T_{DTmax} (°C)	E_{Ae} ($\frac{kcal}{mol}$)	T_{DTmax} (°C)	E_{Ae} ($\frac{kcal}{mol}$)	5 Lutne %	Pozosta- łość smółowa (%)	
I	7 Przyspieszacz	A	110 82	14,5 15,9	147 98	14,2 15,9	14,4 5,1	18 18
		B	80	19,5	88	19,3	5,0	21
		C	92	15,9	105/130	30,5	4,0	35
II	Katalizator	D	90	18,8	125/149	20,1	11,8	36
III	—	113/150	16,9	—	—	23,1	22	
IV	—	90/125	13,8	—	—	58,9	50	

Key: 1 - Coating composition; 2 - TG → vaporization;
 3 - DTA → crosslinking; 4 - TGA; 5 - Volatile %;
 6 - Tar residue (%); 7 - Accelerator; 8 - Catalyst

Table 4

1 Zestaw powłokowy			2 Skład	
I	Przyspieszcz	10	Zywica 1821 + utwardzacz XB 2883	3
			Zywica 1821 + utwardzacz XB 2883 + przyspieszcz tiocykloheksylenoglikol (A)	4
		11	Zywica 1821 + utwardzacz XB 2883 + przyspieszcz oktooino cyny	5
			Zywica 182 + 1772	6
II	Katalizator	D	Zywica 182 + kompleks BF ₃ - amina aromatyczna	7
III			Ciekły poliestr + Cibamin M 100	8
IV			Araldite 6097 + Cibamin H 53 + przyspieszcz kwas p-toluenosulfonowy	9

Key: 1 - Coating composition; 2 - Composition; 3 - Resin 1821 + hardener XB 2883; 4 - Resin 1821 + hardener XB 2883 accelerator thioldiethyleneglycol (A); 5 - Resin 1821 + hardener XB 2883 accelerator tin octoate; 6 - Resin 182 + 1772; 7 - Resin 182 + BF₃ aromatic amine complex; 8 - Liquid polyester + Cibamin M 100; 9 - Araldite 6097 + Cibamin H 53 accelerator p-toluenesulfonic acid

Table 5

TGA: Temperatura rozkładu T_d w °C						
2 Zestaw powłokowy		3 Warunki utwardzania		20 min. 150°	2 min. 250°C	30 min. 120°C
I	Przys- pieszcz	A	370	370	—	
		B	375	375	375	
II	Katali- zator	C	358	360	359	
		D	360	360*)	—	
III	—		370	376*)	—	
IV	—		338	308	—	
			294/330	260/330	—	

* crosslinking 10 min at 200°C

TGA = thermogravimetric analysis

Key: 1 - TGA: Decomposition temperature T_d in °C; 2 - Coating composition; 3 - Hardening conditions; 4 - accelerator; 5 - catalyst

Table 6

1 TSA: Temperatury zeszklenia T _g w °C (TMS):						
2 Zestaw powłokowy		3 Warunki sieciowania		1 h 150°C	1 h 150°C + 15 min. 220°C	15 min. 220°
I	Przyspieszacz	A	86 (58—90)	102 (75—105)	111 (63—146)	
		B	55 (43—62)	69 (51—72)	73 (52—73)	
		C	93 (56—98)	110 (66—124)	118 (61—125)	
II	Katalizator 5	D	83 (64—95)	— (37—81)	98 (64—92)	
III	—		14 (2—39)	3 (—3—33)	1 (—5—29)	
IV	—		99 (80—113)	135 (117—147)	146 (133—152)	

Key: 1 - TSA: Glass temperature T_g in °D (TMS);; 2 - Coating composition; 3 - Hardening conditions; 4 - Accelerator; 5 - Catalyst

Table 7

Properties of base paints on new epoxy compositions

Composition of adhesive	Resin 1821 Hardener XB 2883 Catalyst tin octoate	Resin CY 182 Hardener 1772		
1	2	3		
Ratio pigment/adhesive				
Content of pigment in dry coating	53,5 : 46,5	57 : 43		
Content of zinc chromate	53,5%	57%		
Content of solids at the viscosity of application	20%	20%		
Initial viscosity at application F4, 20°C	75,5%	78,5%		
Viscosity after 7½ hours	27 s	thixotropy		
Viscosity after 24 hours	41 s	thixotropy		
Heating conditions	63 s	thixotropy		
Average thickness of dry coat	10—20 min. 90°C	20 min. 175°C		
Suitability for polishing	42—55 µm	45—55 µm		
	good	good		
Mechanical properties	on bonder 125	on steel plates	on bonder 125	on steel plates
Impact, cmkg, direct	>140	140	180	180
Press according to Erichsen (mm)	1,6	8,3	0,8	0,9
Adhesiveness (DJN 53151)	Gr0	Gr0	Gr0	Gr0
Hardness (Persoz)	—	135	—	155
Saline chamber (ASTM B117) 240 hours	excellent	very good	excellent	good
Spreading of rust (DIN 53 167)	Ri0	Ri0	Ri1	Ri1
Degree of rusting (DIN 53 210)	<0,25mm	≈2 mm	<0,25mm	≈3 mm
Degree of blistering (DIN63209)	Ri0	Ri0	≈Ri1	≈Ri1
Test for tropical conditions (SK DIN 500 17)	m₁/g.	m₂/g.	m₁/g.	m₂/g.
Spreading of rust (DIN53167)	500 hours	500 hours	500 hours	500 hours
Degree of rusting (DIN 5321)	0 mm	0 mm	0 mm	<1/4 mm
Degree of blistering (DIN53209)	Ri0	Ri0	Ri0	Ri0
Resistance to water after immersion (Ford FLPM-EU-BI)	m₁/g.	m₂/g.	m₁/g.	m₂/g.
Loss of adhesiveness (DIN53151)	480 hours	480 hours	480 hours	480 hours
Degree of blistering	Gr0	Gr2	Gr0	Gr1
Loss of gloss	Gr0	Gr4	Gr1	Gr4
	m₁/g.	m₂/g.	m₁/g.	m₂/g.
	a)	a)	a)	a)
	b)	b)	b)	b)
	a)	a)	a)	a)
	b)	b)	b)	b)

a)base coat; b)with top layer,het 30min/130°C

a) base coat; b) with top layer, het 30min/130°C

Table 8

Suitability of new epoxy compositions as bases for coil-coating

Paint components	Resin 1821 Hardener XB 2883 Catalyst tin octoate	Resin CY 182 Hardener 1772										
Parameters of crosslinking	<table><tr><td>3 min. /250°</td><td>3 min. 250</td><td>1 min. /250°</td><td>3 min. /250°</td><td>3 min. /250°</td></tr></table>		3 min. /250°	3 min. 250	1 min. /250°	3 min. /250°	3 min. /250°					
3 min. /250°	3 min. 250	1 min. /250°	3 min. /250°	3 min. /250°								
Thickness of dry coat, μm	<table><tr><td>20</td><td>16</td><td>17</td><td>17</td><td>25</td></tr><tr><td>2 T</td><td>2 T</td><td>2 T</td><td>2 T</td><td>2 T</td></tr></table>		20	16	17	17	25	2 T	2 T	2 T	2 T	2 T
20	16	17	17	25								
2 T	2 T	2 T	2 T	2 T								
Elasticity by T-Bend method (ECCA method)												
Adhesiveness after stamping (pressing) 4 mm with Erichsen apparatus	Category I (without loss of adhesiveness)											
Test for MEK rubbing	200 x											
Resistance to salty fog (ASTM B117, 1000 hours)	no trace of corrosion, no blisters											

Base: 0.7 mm Aluman plates, subjected to action of Alodine 1200

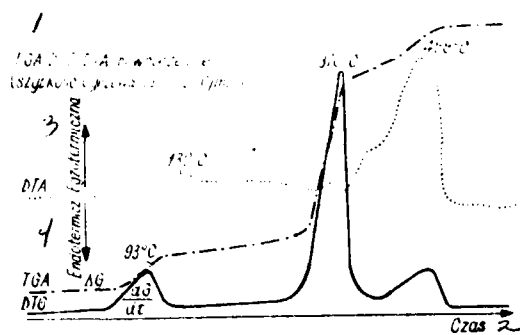


Figure 1. Thermal analysis of composition I (without accelerator)

Key: 1 - Simultaneous TGA, DTG, DTA (rate of heating $\beta = 2^{\circ}\text{C}/\text{min}$);
 2 - Time; 3 - Exothermic; 4 - Endothermic

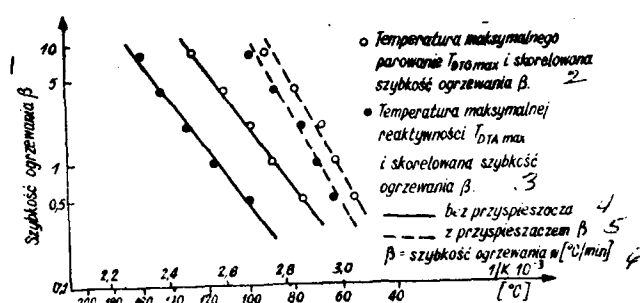


Figure 2. Activation graph of composition I

Key: 1 - Rate of heating β ; 2 - o Temperature of maximal evaporation $T_{DTG \max}$ and correlated rate of heating β ; 3 - o Temperature of maximal reactivity $T_{DTA \max}$ and correlated rate of heating β ; 4 - without accelerator; 5 - --- with accelerator β ; 6 - β = rate of heating $^{\circ}\text{C}/\text{min}$



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completed chemical studies at the Polytechnic in Zurich, where also he obtained doctorate in 1948. Worked in the Institute for Testing Materials in Zurich, in the AWA company in Austria, and in the Swiss paints and lacquers industry. Since 1971 works for Ciba-Geigy AG in Basel in polymer field. Specializes in development of new materials for lacquer products with small content of organic solvents.



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completed chemical studies at the Polytechnic in Zurich, where also he obtained doctorate in the field of polymers. Worked in Micafil company in Zurich dealing with problems of insulating materials. Since 1961 has been working for Ciba-Geigy AG, first as Head of Material Testing Department and now as Head of Polymer Physics Department.

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