

Polyurethane Wire Enamels

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Abstract A short introduction in the history and chemistry of polyurethanes is given. The milestones of the polyurethane wire enamel development are shown, before the general composition of a polyurethane wire enamel was explained. The technical aspects of the isocyanate cross linker and the polyester polyol were described. The solvent system and catalysis were explained. After the discussion of the recipe the processes in the enamelling oven were described. An overview of the Altana polyurethane wire enamel products was given at the end.

Key words polyurethane, wire enamel, TDI,MDI, isocyanate, polyol

1 History and introduction of polyurethanes

Polyurethanes are Polymers containing urethane groups (-NH-CO-O-). A urethane is a reaction product of an isocyanate and alcohol (hydroxy compound) (Fig. 1). This type of reaction was found in 1849 by Wurtz using aliphatic monofunctional isocyanates and alcohols. The hydrogen of hydroxyl group added to the nitrogen atom of the isocyanate group. This reaction is quantitative and without any by-products.

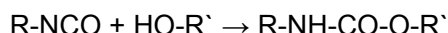


Fig. 1 Urethane formation

The chemistry of polyurethanes starts with the transfer of this reaction type to poly functional educts by O. Bayer in 1937 [1-7]. He creates for this reaction the name poly addition reaction, like it is called today. Additionally to the at that time known ways to polymers, the poly condensation and polymerisation, the poly addition opened a new way to high molecular weight macro molecules (Fig. 2).

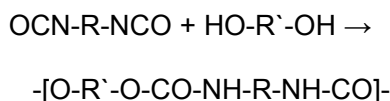


Fig. 2 Poly addition reaction

Using higher functional educts, this means isocyanate and hydroxy compounds having a functionality higher than two, branched and cross linked products were obtained. The high reactive isocyanate can react with every compound carrying acid hydrogen atoms. The reaction with amines leads to ureas, with carboxylic acids amides were obtained (Fig. 3). Also the reaction product, e.g. polyurethane, can react with the isocyanate to get an allophanate cross linked polyurethane. The reactivity of the isocyanates and the big range of possible reactions make the poly addition reaction to flexible tool to generate different properties of the polymers [8-9].

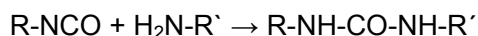


Fig. 3 reaction with amines and acids

2 Milestones in polyurethane wire enamel (PUR-WE) development

The first polyurethane wire enamels were introduced by the Bayer AG in 1950. These wire enamel had the thermal class A and B. This means they had a thermal index higher than 130°C.

In the mid 1970s the company Wiedeking, a daughter of the Altana AG, developed the first class F polyurethane wire enamel having a thermal index higher than 155°C. Also Wiedeking was the inventor of the first class H polyurethane wire enamel with a thermal index higher 180°C in the mid 1980s. Today class B PUR-WE played not big rule anymore, only the class F und class H PUR-WE with a higher thermal stability are requested from the market.

3 The polyurethane wire enamel recipe

Polyurethane wire enamels are used world wide and delivered from the Altana AG and other all over the world. A huge range of different PUR-WE with different properties to fulfil all the costumers' wishes were available at Altana AG. In general the varnish consists out of the following components:

- Isocyanate cross linker (blocked)
- Polyester polyol
- Solvents
- Catalysts
- Additives

Each of this components will described in the following to learn, how the technology of a polyurethane wire enamel works.

3.1 Isocyanate cross linker (blocked)

For the PUR-WE aromatic isocyanates are used, because of their higher thermal stability and reactivity compared to the aliphatic ones. These are mainly 4,4'-Diphenylmethane diisocyanate, MDI (Fig. 4) (also higher functional (Fig. 6)), 2,4-toluylene diisocyanate, TDI (Fig. 5) and its trimer (Fig. 7).

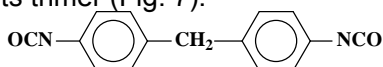


Fig. 4 MDI

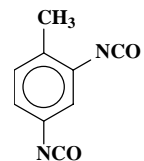


Fig. 5 TDI

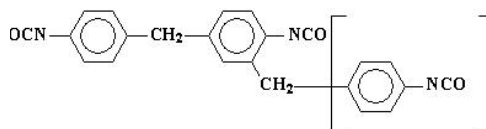


Fig. 6 Poly-MDI

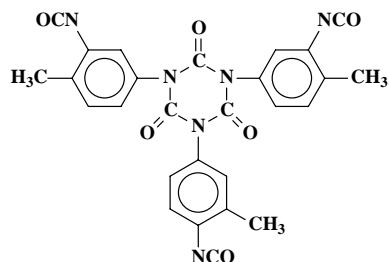


Fig. 7 TDI-trimer

The pure MDI and TDI were not used pure in the WE formulations. They will reacted with an higher functional alcohol like 1,1,1-trimethylenol propane (TMP) in ratio to the diisocyanate of 1:3. Only one isocyanate group in the average is reacted with the hydroxyl group of the alcohol to have still free isocyanate groups (Fig. 8). This was done for three reasons. This pre reaction increased the molecular weight, the branching density and the functionality, which is suitable for a good cross linking of the wire enamel. The handling of this isocyanate adduct is more comfortable and with this step the steam pressure of the monomeric isocyanates, which may cause irritations, was reduced. Almost no free monomeric isocyanates are left in the enamel.

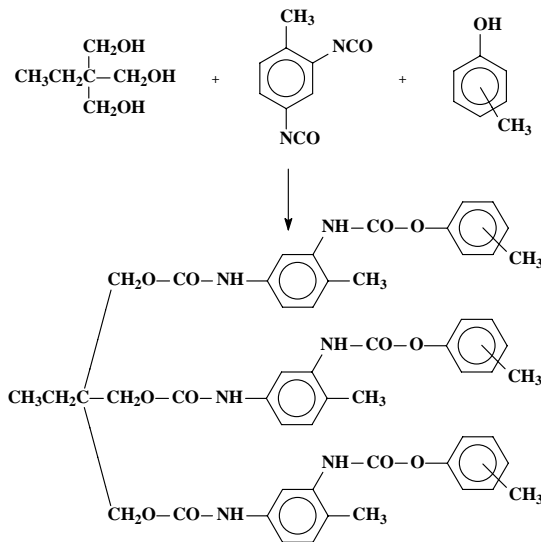


Fig. 8 Isocyanate adduct formation and blocking

the solder ability of polyurethane wire enamels.

In the same step the remaining free isocyanate groups were blocked with an aromatic alcohol (Fig. 8). These blocking agents are mainly cresylic acids and phenols, but also other compounds like caprolactame, malonic esters etc. can be used. The free isocyanates must be protected to obtain a stable one component formulation. In the other case the reactive isocyanate group reacts with the other components in the WE formulation already at room temperature. The obtained blocked isocyanate adduct is the component, which is used in the WE formulations. The TDI-trimer (Fig. 7) was also blocked with cresols or phenols. As blocking agents aromatic alcohols were used, forming with the isocyanate adduct a urethane, because of their low deblocking temperature. The blocked adduct deblocked at a temperature of approx. 120-130°C (Tab. 1). The WE is stable at room temperature, in the oven the deblocking occurs and the free isocyanate groups react with the polyester polyol. The split product (blocking agent) was then evaporated and disappeared from the equilibrium. The splitting of the urethane groups at higher temperature is also the reason for

Table 1 Deblocking temp. of urethanes

| Urethane | Deblocking temperature |
|---------------------|------------------------|
| Alkyl-NH-CO-O-Alkyl | ca. 230-250°C |
| Aryl-NH-CO-O-Alkyl | ca. 200°C |
| Alkyl-NH-CO-O-Aryl | ca. 180°C |
| Aryl-NH-CO-O-Aryl | ca. 120-130°C |

3.2 Polyester polyols

The reaction compounds of the isocyanates in polyurethane wire enamels are polyester polyols, or short polyesters (PE). They were synthesized in a poly condensation reaction of di- or trifunctional alcohol with di- or trifunctional carboxylic acids (Fig. 9) [8-11]. The alcohol compound was used in excess to obtain polyesters with OH-endgroups for the reaction with isocyanate. The water as the poly condensation by-product was removed in vacuum. The process and the product was controlled and adjusted by the acid number and viscosity.

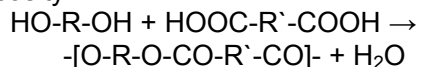


Fig. 9 Polyester

For the polyesters normally glycerin (Fig. 10), TMP (Fig. 11), ethyleneglycol (EG, Fig. 12), diethyleneglycol (DEG, Fig. 13) as alcohols and dimethyl terephthalic acid (DMT, Fig. 14) and trimellitic acid anhydride (TMA, Fig. 15) as carboxylic acid were used.

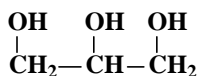


Fig. 10 Glycerine

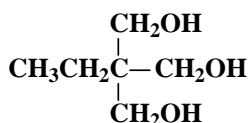


Fig. 11 TMP

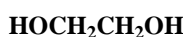


Fig. 12 EG

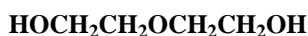


Fig. 13 Diethyleneglycol

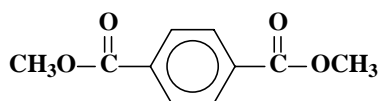


Fig. 14 DMT

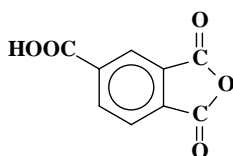


Fig. 15 TMA

Using higher functional (higher than 2) educts branched polyesters were obtained. Highly branched polyesters possess a higher hardness and a good chemical resistance, whereas less branching leads to polyesters with improved flexibility. This is also valid for the resulting polyurethanes. For the

class F and class H polyurethane wire enamels with a higher thermal stability the polyesters were modified with imides. In the wire enamel formulation an excess of the polyester polyol regarding the isocyanate content was used. The remaining free OH-groups are important for the adhesion to the copper surface.

3.3 Solvents

In the wire enamel formulations not only one solvent is used, but a mixture of solvents to obtain a boiling curve (not a boiling point) over a bigger temperature range for a smooth surface of the enamelled wire. Mixing solvents with different viscosity and boiling range, the solvent system was adjusted for each product. The major solvents used for PUR-WE are cresylic acids, phenols, xylene, solvent-naphtha.

3.4 Catalysts

For polyurethane wire enamels two types of catalysts were used. *Tert.*-amines lowered the reaction enthalpy and increased the reaction speed by opening a new way of the hydrogen transport. Metalcarboxylates formed a complex with the reaction partners and lowered the reaction enthalpy and increased the reaction speed that way. For deeper information about the mechanism, see [12].

4 From the wire enamel to the enamelled wire

Knowing the composition of the general wire enamel the processes during curing can be better understood. The application of the enamel can be done by felts or dies. The wire with the liquid enamel runs through the oven. First the viscosity of the enamel decreased due to the high temperature in the oven. The solvents start to evaporate where through the viscosity increased again.

The isocyanate adduct were deblocked and the cross linking with the polyester polyol occurs. The blocking agent diffused to the enamel surface and evaporates with the solvents. The low deblocking temperature and the high reactivity of the isocyanate is the reason why lower oven temperatures compared to other wire enamels were possible. The higher diffusion speed of the phenol or cresol compared to ethylenglycol using polyester or polyester imide wire enamels allowed the higher enamelling speeds.

5 Altana PUR-WE product overview

Altana offers our costumers a hudge range of polyurethane wire enamels with different properties. The products were in this paper divided into the companies, where they were developed, but every product can be supplied from each Altana company all over the world. All products in these tables can be obtained in different viscosities and solid contents. For detailed information, please see our catalogue.

Table 2 Beck Electrical Insulation GmbH products

| Product | Diameter Range [mm] | Thermal Index [°C] | Wire Diameter [mm] | Heatshock IEC [°C] | Cut through Lüscher / IEC [°C] | Tangent Delta [°C] | Solderability [sec / °C] | Comments |
|------------|---------------------|--------------------|--------------------|--------------------|--------------------------------|--------------------|--------------------------|---|
| WE 1332 | 0.02-0.50 | 158 | 0.15 | 180 | 220 / 210 | 150 | 3 / 320 | Fast soldering, UL, pinhole resistant |
| WE 1340 | 0.02-1.00 | 171 | 0.15 | 180 | 230 / 210 | 160 | 8 / 320 | Pinhole resistant, UL |
| WE 1356 | 0.30-2.00 | 157 | 0.8 | 170 | 250 / 230 | 150 | 9 / 320 | Good adhesion, flex., UL |
| WE 1360 | 0.02-0.80 | 174 | 0.15 | 180 | 250 / 245 | 155 | 1.5 / 375 | Good thermal stability, UL |
| WE 1380 | 0.02-1.70 | 195 | 0.15 | 200 | 265 / 250 | 180 | 2 / 375 | High performance, UL, pinhole resistant |
| WE 1380 HD | 0.50-2.00 | 195 | 0.8 | 200 | 270 / 260 | 195 | 3 / 375 | |

Table 3 Deatech products

| Product | Diameter Range [mm] | Thermal Index [°C] | Wire Diameter [mm] | Heatshock IEC [°C] no stretch 1d | Cut through IEC [°C] | Tangent Delta [°C] | Solderability [sec / °C] | Comments |
|---------------|---------------------|--------------------|--------------------|----------------------------------|----------------------|--------------------|--------------------------|---|
| Deaweld S 132 | 0.03-1.00 | 155 | 0.1 | 175 | 240 | 160 | 0.5 / 360 | Fast soldering, pinhole resistant |
| Deaweld S 193 | 0.02-1.00 | 182 | 0.1 | 200 | 260 | 180 | 2 / 360 | High thermal stability, pinhole resistant |
| R 77 | 0.03-2.00 | 155 | 0.1 | 175 | 240 | 160 | 2 / 360 | Good flexibility |
| R 83 | 0.03-1.00 | 182 | 0.1 | 200 | 250 | 170 | 2 / 360 | High thermal stability |

Table 4 P.D. George products

| Product Solderite | Diameter Range [AWG] | Thermal Index [°C] | Wire Diameter [mm] | Heatshock NEMA 3d 20% stretch | Cut through Lüscher / NEMA [°C] | Tangent Delta [°C] | Solderability [sec / °C] | Comments |
|-------------------|----------------------|--------------------|--------------------|-------------------------------|---------------------------------|--------------------|--------------------------|-------------------|
| A 928 | 18-44 | 163 | 0.51 | 175 | 240 | 155 | 3 / 360 | Fast soldering |
| B 794 | 14-28 | 173 | 0.51 | 175 | 245 | 135 | 5 / 360 | General purpose |
| L 9379 | 18-44 | 169 | 0.51 | 175 | 262 | 160 | 5.5 / 360 | Pinhole resistant |
| M 932 | 18-44 | 159 | 0.51 | 175 | 243 | 148 | 4 / 360 | Fast running |
| Isomelt 11022A | 12-36 | 161 | 0.32 | 175 | 235 | 132 | 3 / 360 | Pinhole resistant |

Table 5 Tongling Siva products

| Product | Diameter Range [mm] | Thermal Index [°C] | Wire Diameter [mm] | Heatshock IEC [°C] no stretch | Cut through IEC [°C] | Tangent Delta [°C] | Solderability [sec / °C] | Comments |
|-----------------|---------------------|--------------------|--------------------|-------------------------------|----------------------|--------------------|--------------------------|---|
| Tongsold 215 | 0.10-1.50 | 180 | 0.5 | 200 | 260 | 166 | 4 / 375 | Pinhole resistant (JIS), high speed enamel |
| Tongsold 246 | 0.02-0.80 | 155 | 0.5 | 180 | 260 | 160 | 2 / 375 | Pinhole resistant, good runability |
| Tongsold 246 LS | 0.02-0.80 | 155 | 0.5 | 180 | 220 | 135 | <4 / 330 | Pinhole resistant, good runability, solderable at 330°C |
| Tongsold 240 | 0.02-1.20 | 155 | 0.5 | 180 | 250 | 160 | 1 / 370 | Pinhole resistant, good runability, fast soldering |
| Tongsold 220 | 0.02-1.20 | 155 | 0.5 | 180 | 240 | 130 | 1 / 370 | Pinhole resistant, fast soldering, no residual |

The WE 1332 is a very fast soldering class F PUR, which is pinhole resistant. A high performance class H PUR-WE with a high thermal stability is the WE 1380, pinhole resistance. The R 77 showed good flexibility, the Solderite M 932 is a fast running PUR. The Tongsold polyurethane wire enamels having a outstanding pinhole resistance and have a good run ability.

6 Current developments

To keep the leading position in PUR-WE a lot of work will be done in the R&D laboratories. Just to name a part of the

running projects, the researchers of Altana trying to reduce the stack loss of PUR-WE. The resulting enamel will be more efficient. Using the same enamel in the same amount, more enamelled wire can be produced. Through modification of the solvent system and resin modification the enamelling speed of PUR-WE should be increased. Together with this issue, alternative solvents, which are in the ideal case cheaper than the existing solvents and ecological friendly, are under investigation. Also the development of class 200 and class 220 PUR-WE will be done.

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