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Advances in monomer free unsaturated polyester technology

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In meanwhile more than 10 years many experiences in the processing of monomer free unsaturated polyester resins (in the following also referred to as MF resins) were gathered. 10 years, in which new types were developed and successfully introduced into the market. At present MF resins are used in all areas of electrical devices.

It was a decade in which the comparatively young group of unsaturated polyester resins gained market maturity, a good reason for a review on the history of the MF resins and the presentation of new insights.

30 years ago…

It was back in 1978 when Dr. Günter Hegemann, former director of R&D for trickle and impregnating resins at Dr. Beck GmbH, started investigations on substitutes for styrene, the most common monomer in unsaturated polyester resins. He closed with the conclusion that although alternative monomers exist, eventually their advantages were eliminated by serious disadvantages. The logical consequence has been the development of a new type of unsaturated polyester resins for which no monomers were used at all. Despite this recognition it still took some years before the development finally started.

In cooperation with BASF Ludwigshafen a team of scientists started research to realize the idea of a monomer free unsaturated polyester resin. Finally, in 1996 the research came to a successful result. The first monomer free trickle and impregnation resin based on unsaturated polyester, Dobeckan® MF 8001 was introduced into the market. It met great interest at several users due to its environmental, health and safety benefits and its mild odour. Concern with respect to the resins viscosity of 30.000 mPas prevented the resins success. It was the successor product Dobeckan® MF 8001 NV, that in the end was the first triumph for the new group of unsaturated polyester resins. With this version the viscosity was reduced significantly down to 7.500 mPas and new applications were entered.

Dobeckan® MF 8001 NV was not just the first commercial success for MF resins but more important an affirmation for a whole approach and first proof that the MF technology will have a great share in the supply of electrical insulation resins. Further developments which met particular market needs followed and resulted in a comprehensive portfolio of monomer free resins.
Currently 6 groups make the MF portfolio, as shown in table 1.

Dr. Hegemann's report on the substitution of styrene was published in beck isolier technik, issue 53 from1978

Table 1:

Name Dobeckan®	Description	Use
MF 8001 NV MF 8001 UV-2	Polyester; Elastic, environmentally friendly product for general purpose use	Stators of motors and generators Transformer
MF 8004	Polyester-imide Tough-elastic, environmentally friendly product for applications with high maximum thermal and mechanical loads	Alternator Servo motor
MF 8044 MF 8044 UV	Polyester-imide Tough-elastic, environmentally friendly, high reactive product for applications with high maximum thermal and mechanical loads	Generator Power tools Special applications
MF 8005	Polyester; Elastic, environmentally friendly product with very low viscosity, general purpose use	Small transformer Universal drive
MF 8006	Polyester-imide Elastic, environmentally friendly, high reactive product for applications with high maximum thermal and mechanical loads	Generator Transformer Special applications
MF 86..	Polyester/Polyester-imide Tough-elastic, environmentally friendly, product with superb thermal conductivity	Drive Generator

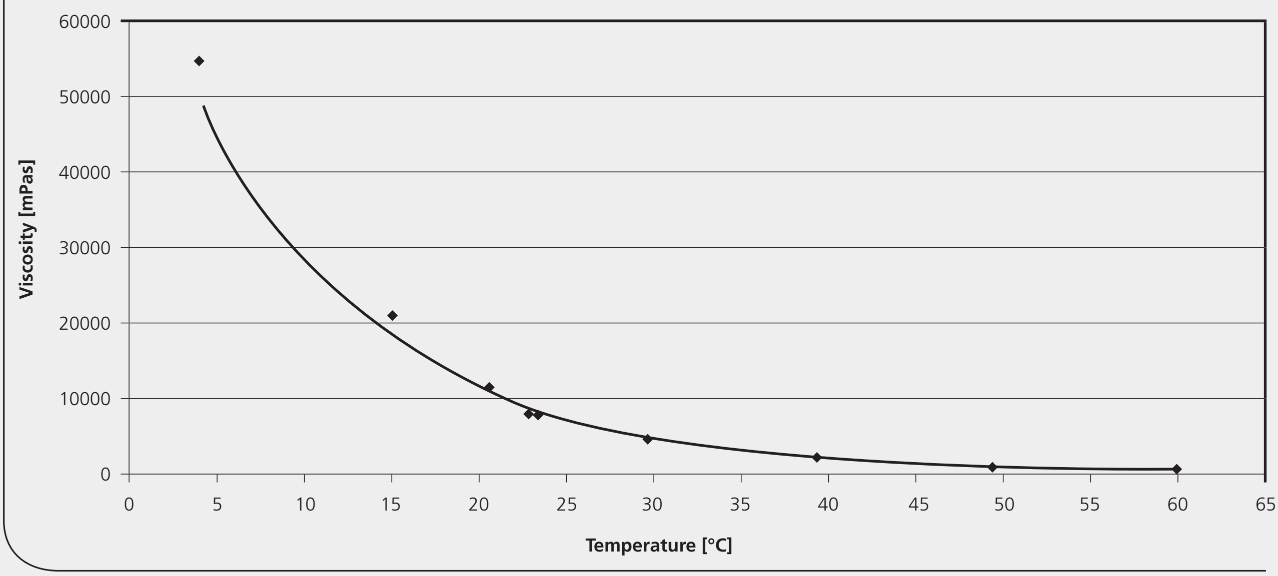
Viscosity and Penetration of MF Resins

As no monomers with very low viscosity are used for MF resins, this group of electrical insulation systems is higher in viscosity than conventional resins. Very often this fact is being used as an argument against monomer free resins and equated to with bad penetration properties. At first the relation between viscosity and penetration seems logical, but certainly the penetration of a resin into a winding structure does not depend only on its viscosity. On the contrary other properties must be considered also.

As a kinetic factor, the viscosity is a measure of the resistance of a fluid to being deformed. The viscosity is equivalent to the reciprocal value of the fluidity. A higher viscosity is often perceived as a greater thickness of a liquid, which is caused by molecular friction in movements relative to each other. This results in cohesion of the fluid and its resistance against deformation. The larger the molecules are, the higher the friction and the stronger the resistance against deformation. Hence the viscosity of the small monomers like styrene, vinyltoluene, diallylphtalate and diacrylate is low compared to the large polymers of the polyester based resin.

Molecular motion is higher at elevated temperatures. With the increased mobility of each molecular fraction the fluid viscosity drops. Illustration 1 shows the viscosity of Dobeckan® MF 8044 dependence on the temperature.

Ill. 1: Viscosity-temperature-graph of Dobeckan® MF 8044



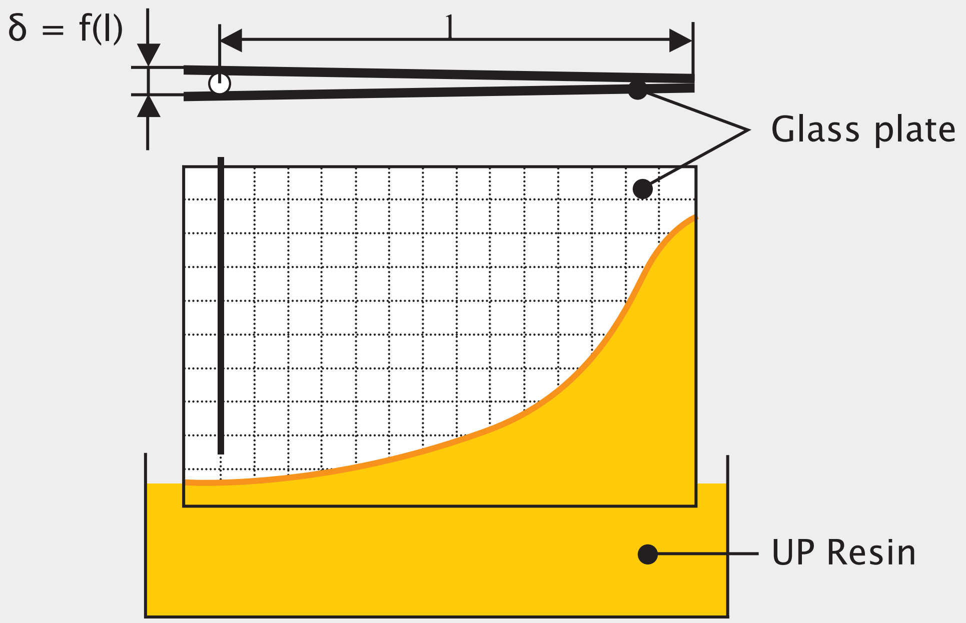
Resins are able to penetrate a winding structure as a result of two mechanisms. Initially resin flows into the structure due to the relative speed of resin and the part and the tendency of the resin to keep its energetically favourable form. In fine structures, the capillaries, the resin is also sucked upwards against gravity. The cause of this movement, known as the capillarity effect, is surface tension between fluid and solid substrate. The dependence is well expressed in the equation for the penetration height in capillaries:

$$h = \frac{2\sigma \cdot \cos\varphi}{\rho g r} \quad \{1\}$$

h: penetrated height
σ: Surface tension
φ: Contact angle
ρ: Density of fluid
g: Gravity acceleration
R: Radius of capillary

By implication, the thermodynamic factor, surface tension and the contact angle, help to assess a resins ability to penetrate winding structures.
Stators used as a standard for processing tests the MF resins were found to have very good pene-tration.. Despite the high viscosity it was seen that even small capillaries were completely filled with resin. Hence experiments in the application department laboratory of ELANTAS Beck GmbH were conducted to compare the ability of monomer free resins and conventional resins to penetrate small structures. The confirmation of the very good penetration was gained from an easy but very demonstrative test in which two glass plates were bonded together. At the one end, a wire with 1 mm thickness was laid in between the glass plates so that a gap with the size d occurred. Depending on the distance from the wire this gap got thinner unless it was completely closed at the opposite side (see illustration 2).

Ill. 2: Set up of test for demonstrating the penetration of capillaries



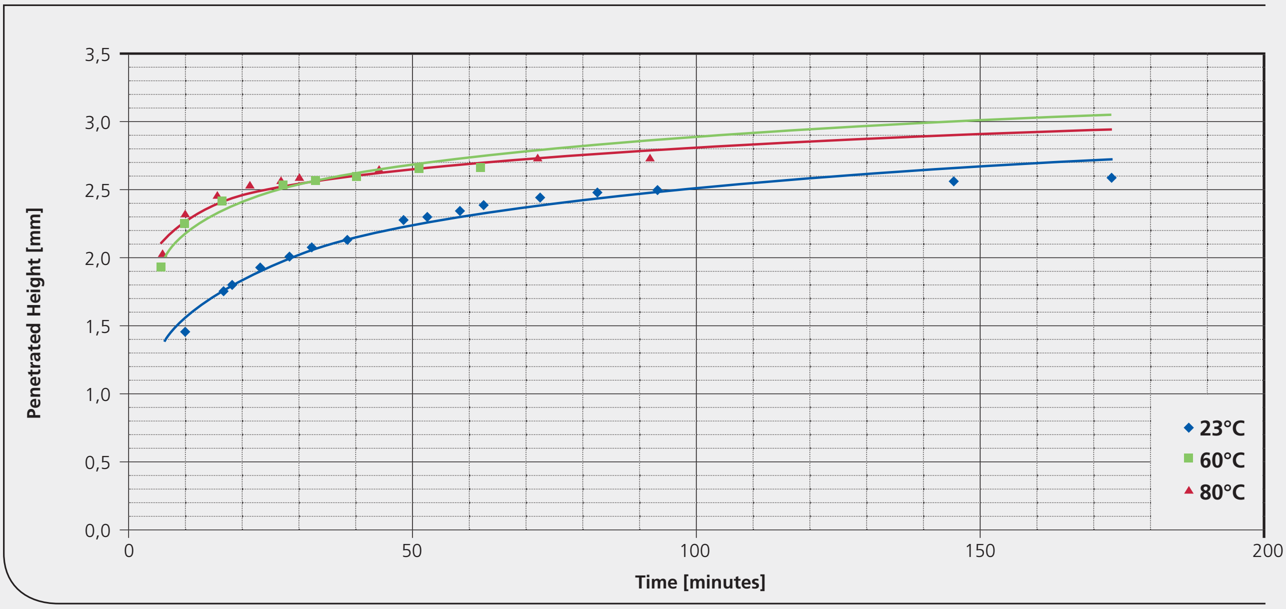
The plates were put into the resin at a defined depth. A grid on one of the plates was used to de-termine the penetrated height depending on the distance to the wire. Knowing the distance it was possible to calculate the gap length with equation 2.

$$\delta(l) = 1 \cdot \sin\frac{D}{21'} \qquad \{2\}$$

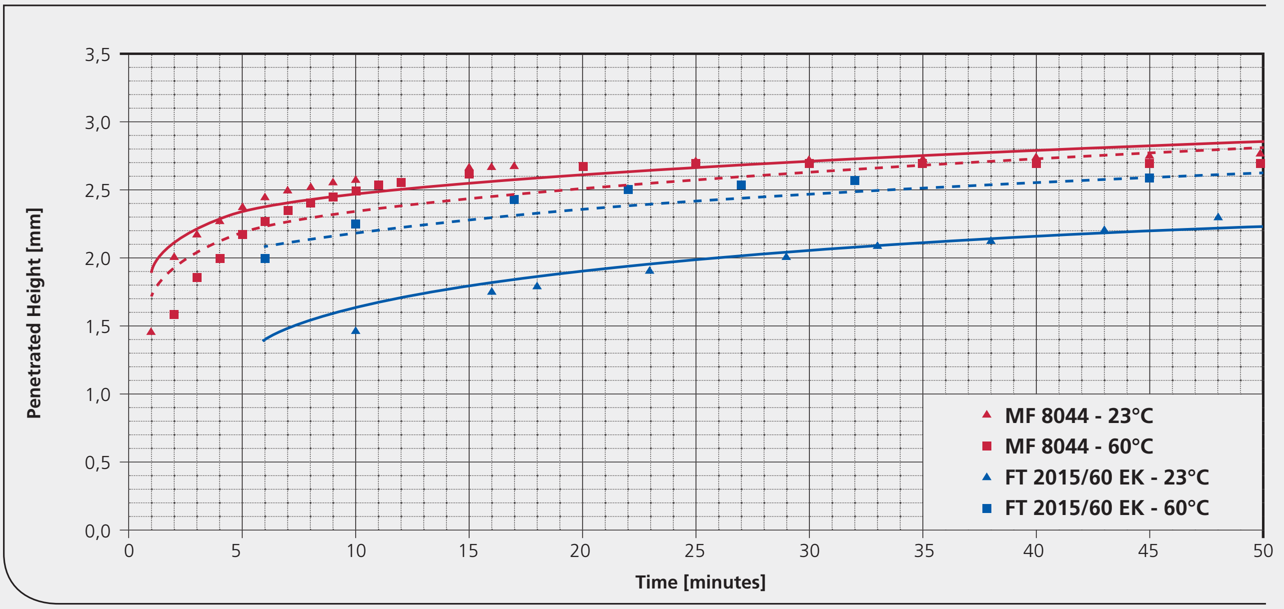
δ: Gap length
l: Distance from the wire
D: Wire diameter (reference gap length)
l': Horizontal gap length

For the determination of the temperature dependence the whole set-up was put into an oven. After thermal equilibrium was achieved, the test was started by immersing the glass plates into the resin. The test results are shown in the illustrations 3 and 4.
The first picture illustrates the varying penetration at different temperatures of Dobeckan® MF 8044. It can be seen that the penetration is faster at higher temperatures, which is achieved by pre-heating the parts, whereas the stationary values are almost equal. Furthermore this graph shows the limit of pre-heating parts to improve the resins penetration into the winding. At temperatures above 60°C the effect is negligible. Both curves, measured at 60°C and 80°C respectively, are almost identical. Thus further pre-heating results in neither a better nor a faster penetration of the winding.
Compared to the significantly less viscous Dobeckan® FT 2015/60 EK, the findings of the first test are confirmed. The penetration of the conventional resin initially is better, it penetrates the winding faster. There is almost no difference between the penetration heights at 23°C and 60°C due to the lower surface tension of the Dobeckan® FT 2015/60 EK at elevated temperatures. Even though the conventional resin initially penetrates the winding structure faster, the stationary value is practically identical with a warmed MF resin at 60°C. Though the viscosity of Dobeckan® MF 8044 is higher at 60°C compared to the conventional resins viscosity at room temperature 23°C, 435 mPas instead of 250 mPas, the behaviour is equal due to the better surface tension and the higher contact angle.

Ill. 3: Penetration height into a slot of 1/55 mm Dobeckan® MF 8044 at different temperatures



Ill. 4: Penetration height into a slot of 1/55 mm Dobeckan® MF 8044 and Dobeckan® FT 2015/60 EK



The tests proved that an estimation of a resin's penetration capabilities based only on the viscosity is not acceptable. Almost identical penetrated heights were achieved in capillaries despite the significantly higher viscosity of monomer free resins in some of the tests. This effect can be explained with a higher surface tension and contact angle, compared to unsaturated polyester resins based on monomers.

Increase of Impregnation Efficiency

The above remarks implies that pre-heating parts above 60°C doesn't seem sensible when processing monomer free unsaturated polyester resins. However, processing recommendations for MF resins suggest even higher temperatures, up to 135°C depending on the parts size and construction. This is due to the fact that higher pre-heating temperatures enable an optimized process with respect to winding fill factors, resin consumption and used energy.

The application of conventional, monomer containing resins usually do without pre-heating of the parts. This is prevented by the high volatility of common monomers and concerns with respect to the tank stability. When hot parts are dipped, large amounts of monomers are lost by evaporation. This loss must be compensated by adding monomer to the tank to avoid unacceptable increases of the resin viscosity, hence altering processing conditions with varying impregnation results. A regular tank test is required. Furthermore many conventional systems tend to have continuous polymerization ones the reaction has started. At the very beginning the reaction rate is small, but it increases continually afterwards. Gelling of the resin in the tank is imminent. The monomer free unsaturated polyester resins Dobeckan® MF offer superb tank stability. In practice damage of the resins should not be expected even when parts with high pre-heat temperatures are processed. This fact actually makes a hot-dip process possible and enables the gelling of the resin inside dipped parts.

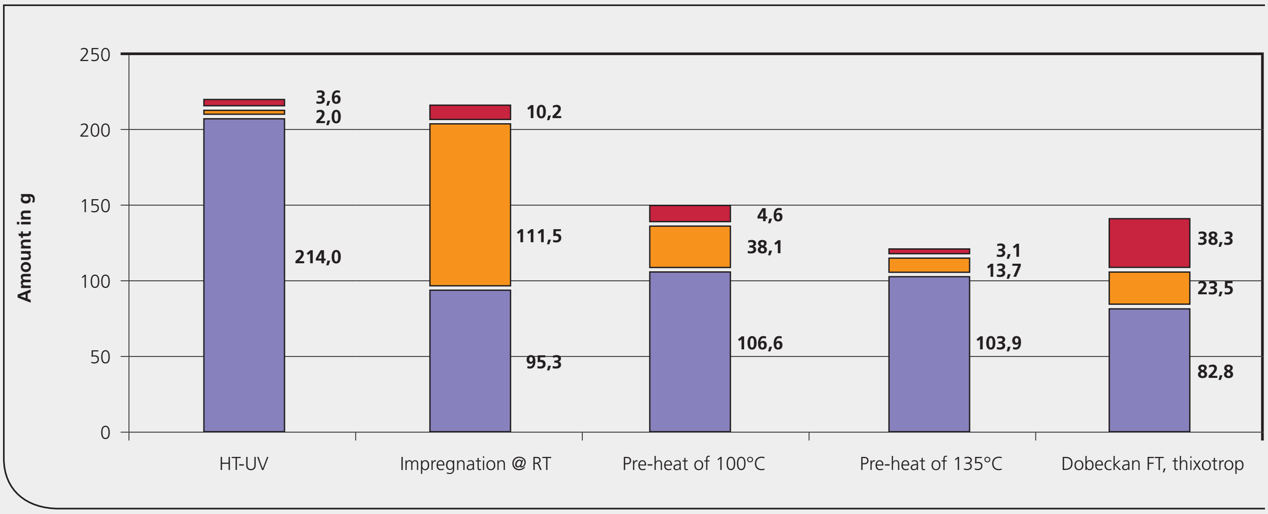
A pre-heat of the part is advantageous in many ways. Due to the higher starting temperature less time is required to cure the parts in the oven. Even though the parts are chilled while dipped in the resin, the temperature is still higher compared to the impregnation at room temperature. The gelling is faster and higher winding fill factors with less secondary drainage are achieved. Of even higher importance is the possibility to gel the resin while the part remains dipped. This process builds cross links between the polyester polymers. With ongoing gelling even more molecules are linked together and even larger particles are formed, which can be observed in the increasing viscosity of a gelling resin. The fluidity of the resin decreases continually and associated with the decrease of fluidity the secondary drainage in the curing oven is reduced as well. The resin that does not drains off the part remains in the winding and helps to increase the impregnation quality and the properties of the parts also.

Pre-heating the parts and keeping their higher temperature to gel the resin during the immersion can be considered as the optimal process. The filling of the winding can be controlled by simple variation of dipping time or dipping temperature and the results achievable are comparable to a roll dip process.

Investigations were made in the laboratories of ELANTAS Beck GmbH to determine the impregnation efficiency of different processing. The following illustration 5 breaks down the resin consumption into three segments: the evaporation losses, the secondary drainage and the remaining resin in the winding after cure. All results are based on tests with a 4 pole stator for standard use in size 90. Resins used were Dobeckan® MF 8044 as well as the thixotropic Dobeckan® FT 1052/60 EK, optimised against drainage.

As the first column shows the hot-dip with gelling of resin during dip (HT-UV) is able to fill the winding completely in an electrical machine. A fully filled winding guarantees significantly better thermal conductivity due to the avoidance of trapped air. A customer proved the advanced thermal conductivity in a load test, where pump stators were impregnated by trickling with a styrenated conventional resin and hot-dipping in Dobeckan® MF 8044. During the load test the temperature rise of the trickled stator went up to 125°C and that of the MF impregnated, fully filled winding went up to only 89°C even though both performed identically. In addition to better performance, highly filled windings show better thermomechanical properties and are less vulnerable to humidity and destruction by chemicals.

Ill. 5: Impregnation efficiency of different methods and resins (Dobeckan® MF 8044 and Dobeckan® FT 1052/60 EK)



Winding fillings achievable without pre-heating are very similar to the results of the conventional impregnation. When the parts are moved into the oven, the resin reduces viscosity with increasing temperature and evidently is sucked into the winding. However, the larger amount of excessive resin on the parts surface causes high secondary drainage, so that this processing is not recommended except for the low viscous Dobeckan® MF 8005.

A reduction of secondary drainage is already being achieved at dip temperatures of 100°C for small parts, as shown in the third column and even lower temperatures for larger parts. The improved penetration combined with a faster gelling in the oven reduces the total losses to a smaller extent compared to drainage optimized conventional resins. Nevertheless, the winding is more completely filled and better properties of the device are achieved.

A further optimization is possible even with small sized parts as long as they are pre-heated to higher temperatures. In tests a pre-heat of 135°C was investigated. With such a treatment before impregnation the total consumption can be reduced to values below the consumption of thixotropic impregnating resins with monomers and coincidentally the filling can be increased. Lower evaporation losses and even significantly lower secondary drainage make this process more efficient without fearing that the resin is damaged.