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The thermocured compositions have found broad application in the electrotechnic industry: coverings copper mouting wires (enamel wires), printed circuit boards, electrotechnic contacts, and also in filling compounds (used in transformers), etc. Compoundings, ways of receiving of thermosetting compositions received with use of epoxies, and also application and properties of the received varnishes on their basis are given in this review.

Key words: epoxy, alcohols, amines, acids, anhydrides, anhydrides of acids, terpenomaleinic adduct, thermocured compositions.

Introduction. The import of expensive thermosetting polyester, polyamide and polyimide coatings or mixtures for the protection of products from electrical copper are applied in the electrical industry. They include coating copper wires, assembly wires (enameled wires), printed circuit boards, electrical contacts and in the casting compound (used in transformers), etc. In Belarus the main consumers of these paints are of “Gomelkabel” and JSC “Atlant” (Baranavichy). In the Russian Federation they are ZAO “Microwire” and JSC “NP Podolskkabel” (Podolsk), JSC “JV” Volgagmag “(Rybinsk), OOO “TK cable Volga” (Samara). Since insulating varnishes are not produced in Belarus, even though they are export-oriented, the research on the development of new thermoset coatings with improved performance characteristics, and the organization of their production is very relevant.

It is known that epoxy resins (ES) and materials based on them are widely used in various fields of national economy thanks to valuable properties: low shrinkage upon curing, high adhesion to various materials, chemical stability, good physical, mechanical and excellent dielectric properties [1].

ES is used for the manufacture of potting and sealing compounds, putty, structural adhesives, coated films and coatings, binders for fiberglass, cast products, as well as for the manufacture of industrial equipment [1].

At present, the chemical industry of the CIS countries made a wide range of ES: ED-8 (860-1000 M), ED-10 (M 660-860), ED-14 (M 540-620), ED-16 (M 480-540), ED-20 (M 390-430), ED-22 (M is not more than 390), E-40 (M 600), and so on, contributing to the creation on their basis of a variety of curable compositions.

One of the most important areas of application of ES is to obtain on their base lacquers used in various industries, especially electrical ones.

Main part. We have conducted research on patent formulations, methods for preparing the thermoset compositions and properties obtained using ES.

ES in the cured state have a small number of crosslinks which are at a considerable distance from each other, and therefore the segments between the cross-linked chains have some mobility. Consequently, they are less fragile, and differ from other resins of higher flexural strength. Since the transition of the state from fusible and soluble to infusible and insoluble is not associated with the release of any volatile products, cured resins don't form pores and blisters.

The presence of ES in two types of functional groups (the epoxy and hydroxyl) allows the solidification of different substances capable to interact not only with epoxy, but with the hydroxyl groups.

Curing agents are polyols, amines, anhydrides of dicarboxylic acids, dicarboxylic acids, isocyanates, diphenols, various resins, and some other compounds. Some of these steps are connected to ES in an amount approximately equivalent to the content of epoxy groups and others are added to the resin in a small quantity and play a role of catalyst. In both cases, ES are insolubilized having a mesh structure. It depends on the type of curing agent or on the process that occurs at ambient temperature and accompanied by a significant evolution of heat, or require additional heating.

Curing alcohols. According to the paper [1], alcohols can be used as ES curing agents.

The properties of lacquers based on epoxy powder formulations with phenolic hardener are well studied [2]. It is shown that gloss is achieved at a maximum coating thickness of 90–95 microns, it is observed to increase in strength of 80 kV voltage, and the optimal mode rejection is 15 minutes at 180°C.

There is a method of producing an electrically insulating adhesive varnish [3], where curing agent is a mixture of C₁₋₈ dihydric alcohols. This lacquer contains no volatile toxic components suitable for wires of thermal class F. When cured coating is obtained having dielectric strength $E \geq 4$ kV/mm, volume resistivity is $\rho_v \geq 1 \cdot 10^2$ ohm · m.

Wires with electrical insulation were prepared by coating consisting of polioksiefira obtained by

reacting a dihydric phenol with bisphenol ES $SP \leq 10$. The composition is directly applied onto and cured in the wire [4].

Curing amines. Addition reactions of amines with epoxy resins groups are proceeded with great heat release, therefore the manufacture of large products need to use large amounts of filler (e.g., silica flour or asbestos fibers) which improves the conditions of heat removal.

The use of diamines or polyamines provides a denser mesh structure than with the use of amines. Polyamines are highly reactive, low volatility and ability to obtain an anhydrous condition.

Ethylenediamine, hexamethylenediamine, diethylenetriamine, polyethylene polyamine and dicyandiamide are known as the most widely used found curing agents. They are added to the resin in an amount of 5.0–10.0% [1].

This composition [5] is used as the anticorrosive coatings containing ES. The amine hardener is polyethylene polyamine, and a plasticizer is camphor oil.

A epoxy composition [6] which includes a mixture of EC, the amine curing agent and a flame retardant filler.

Modified polyamidoamine, which gives coatings corrosion and chemical resistance, was developed [7] as modified aliphatic amine hardener for fast curing epoxy coatings and low viscosity curing agent.

The epoxy composition was obtained [8], including the EC, polyethylene polyamine hardener, pigment, filler and rapeseed oil was used as a plasticizer.

The properties of an epoxy coating [9], the cured adducts with 1,3-diaminopropane alkylresorcinol (11-DAP) and n-butylglitsidilovym ether (12-DAP) are described below. It is shown that the investigated adducts of bisphenol was cured with epoxy oligomers, forming a chemically resistant coatings with high physical and mechanical properties.

Hardener for aqueous dispersions ES [10] was prepared by first reacting the product of esterification of the original ES polialkilenpoliefirpoliolom with 2-10-fold stoichiometric excess of amine and subsequent reaction of the resulting intermediate with 0,02-0,25 eq. % monoepoxide.

An insulating powder composition [11] containing diene ES, stearic acid, and m-phenylenediamine. Having been cured (at 150–170°C) to form a coating with increased resistance to moisture, it improved its insulating properties and low moisture absorption.

The process of curing compositions was based on ES, the primary hexamethylene diamine and a tertiary amine FOM-9 [12]. It is shown that the use of a composition comprising an amine FOM-9 allows you to reduce the consumption of scarce primary amine and obtain coatings with high mechan-

ical and electrical insulating properties.

It is known [13, 14] that using as a curing agent dicyandiamide ES can be obtained thermosetting electrical insulating varnish of raised temperature resistance with excellent chemical and corrosion resistant, elasticity and adhesion.

The authors used the described method [15] for producing an electrically insulating impregnation varnish with fire resistance class F. The varnish comprises (parts by weight) 100.0 ES with epoksiokv, 170–225 (65–70%), 20–40 mixture of 1 : (1.5–1.38) diaminodiphenylmethane and diaminodiphenylsulfone and ≤ 0.6 amine accelerator.

It is a method of impregnating varnish [16] with the following composition (parts by weight): 70.0–85.0 ES with epoksiokv. 400–500 with the addition of 3 dicyanamide as a hardener, 0,3 dimethylbenzylamine, 15.0–30.0 ES with epoksiokv. 180–200, modified fatty acids when 170–180°C. Varnish occurs at 2.5–3.5 min at 150°C.

Compositions [17] for heat-resistant insulating coating consist of epoksipolisiloksana, dicyandiamide, steklofrity, SiO_2 and redoksayda. The composition forms a coating with high electrical insulating properties at temperatures up to 700°C and strength properties at 100–300°C.

A insulating composition [18] contains diene ES epoksianilinovuyu resin, PA-low molecular weight resins, synthetic pile, granular filler and amino coagent.

To increase the elasticity of insulating coatings on the basis of EC the authors of [19] proposed to use 100.0 pts. wt ES 20.0–25.0 pts. wt PU-rubber (modified PET product diisocyanate). When administered poliefirnoepoksidny electrically insulating lacquer BF3 complex compounds with amines increase their storage stability.

Some physical, mechanical and dielectric properties of coatings based on ES grades E-41 and E-5 with amine curing agents were investigated [20]. It was shown that the coating with good physical and mechanical properties are better to apply with E-41ES mark.

A thermosetting powder material was also used [21]. It's the guanamines and ES coating. ES guaminom reacts to form a non-meltable and insoluble polymer.

A method of producing insulating coatings of polyester and ES was quite successful [22]. The dicyandiamide was used as the hardener, some amount of which corresponds to the content of epoxy.

The prepared hardener [23] is an aqueous solution of 1 : 2 with cyclohexanedimethanol diglycidyl ether diamine (m-ksilendiamin, diamintsiklogeksan et al.).

Curing isocyanates. Isocyanates were used for curing the hydroxyl oligomers and epoxy polymers such as bisphenol epoxy oligomer having a molecular weight M higher than 1,000, of epoxy and

phenoxy resins. The most common curing agent is an isocyanate-based polymer of diethylene glycol and 2,4-toluene diisocyanate [24].

The authors [25, 26] designed for enameled wire insulating composition comprising polyesters ES adding ethylene glycol and glycerol, blocked isocyanates, organic solvents, and curing catalysts.

It is known [27] that the chemical modification of lacquer CN-0125 epoxy and isocyanate oligomers leads to a significant improvement in protective properties of coatings based on it.

Electrical insulation varnish is developed [28] with improved physical and mechanical properties (heat resistance and adhesion), which was prepared by reacting in the medium at 80–120°C solvent mixture consisting of 10–90.0 pts. wt. The polymer has units of bismaleimide, triazine and diisocyanate 10–90.0 pts. wt. The ES molecular weight is $M \geq 500$.

An electrically insulating varnish [29] was received. It formed a coating with high resistance to hydrofluorocarbon refrigerants. The composition of thermosetting compositions includes polyvinyl, ES, PA (the reaction product of a tetracarboxylic acid dialkyl and polyisocyanate) and blocked polyisocyanate.

Epoksiuretan is based on film former and a polyisocyanate hardener composition. It is developed [30] with a high solids content for the protection of metals, engineering plastics and other materials.

The known composition [31] is based on the elastic impact-resistant and moisture-insulating coatings which comprises (parts by weight.): 50.0 of hydroxylated resin and 2.5–50.0 blocked polyisocyanate.

The insulating composition [32] impregnates the winding wire for a fiberglass shell and for bonding a copper wire sheath contains, as film-forming 34.0–48.0 wt PEF% saturated with CN <5, 8.5–12.5 wt ES%, 39.5–57.5 wt % of blocked polyisocyanate 10.0–36.0 wt % xylene.

Curing condensation resins. ES cure various FSF of novolac or resole type administered in the amount of 30.0–60.0 wt % when heated to 160–205°C for 0.5–10 hours [1].

The authors [33] designed epoxy coating compositions containing a mixture of modified EC and 1.0–50.0 pts. wt hardener in the form of the FSF or melamine-formaldehyde resin (MLFS). The compositions form coatings with improved flexibility, adhesion and water resistance.

The obtained compositions [34] contain diane ES with molecular weight $M = 900$ –10,000 with the addition of 5.0–60.0 pts. wt hardener (resole FSF) as film formers. Fast hardening compositions form coatings with high adhesion to metals.

The winding wire with an outer insulating layer is obtained by applying a varnish which is a so-

lution of a mixture 25.0–75.0 pts. wt. The electric and 25.0–75.0 pts. wt with the addition of the FSF 5.0–20.0 wt % imidazole curing agent, and a surfactant has a filler and other additives [35].

In [36] a method for producing a composition for insulating coatings consisting of polyvinyl acetal and parts by weight: 10.0–30.0 ES 24.0–38.0 FSF 36.0–66.0 polyvinylacetat.

To short the drying time, improved physical and electrical properties of the enamel coating developed [37] comprising ES MLFS, urea-formaldehyde resin, butanolizirovannuyu CFF (BFFS), and adipic acid, o-toluic, pigments, fillers and solvents are insulated.

The electrical insulating varnish [38] on the basis of epoxy (EE) and varnishes based on styrene copolymers EE were studied. It was found that the coatings based on combinations of EE and cresols with formaldehyde and MLFS have good physical, mechanical and electrical properties.

The cover [39] with high thermal, moisture and chemical resistance, which is obtained based on compositions comprising a film-forming mixture as PET with a molecular mass $M > 10,000$, with a molecular weight ES $M \geq 5,000$ and CFF was developed.

Curing di- and monocarboxylic acids. The reaction of organic acids with the last ES curing occurs at elevated temperatures.

In the presence of a dicarboxylic acid, this process is much faster than adding monocarboxylic acids. With increasing molecular weight organic acids increased elasticity curable ES [1].

The thermosetting composition of low temperature hot melt based on a mixture of EC and polycarboxylate hardener (polycarboxylic acids, their anhydrides) have become widely known [40].

Curing anhydrides of dicarboxylic acids. Alongside carboxylic acids as hardeners ES used dicarboxylic acid anhydrides. The reason is that the reaction with the alcohol group resin anhydrides unlike mono- and dicarboxylic acids, water separation occurs and the formation of by-products [1].

A high quality hardener ES [41] is an acid di-anhydride benzophenone.

A method for obtaining the anhydride curing epoxy compositions [42] with the addition of a polybutadiene adduct of maleic anhydride (MA) was used. Such compositions are cured at 80–120°C first, and then at 200–300°C to form the final product with improved mechanical properties and $T_g = 250$ –350°C.

The thermosetting composition of [43] for the insulating coating, which has the following composition (wt %): 10.0 ES 2.0–40.0 epoxidized poly-1,2-butadiene monomer 1.0–10.0 (dimethylstyrene or (meth) acrylic acid) and 10.0–50.0 MAK is now well known.

A method for curing ES carboxylic anhydride [44] in the presence of a curing agent obtained by reacting imidazole or a derivative thereof and an organic ester of boric acid was disclosed.

The following insulating composition [45] was used (wt %): 10.0 the binder (mixture of 3.0 and 7.0 cycloaliphatic bisphenol ES), 20.0 of the inorganic filler, the inorganic dispersant is 0.5, 0.2 and 40.0 MA a complexing compound, and the rest. They were used as the solvents.

The phthalic, hlorendikovy, methyltetrahydrophthalic, tetrahydrophthalic anhydride, and some mixtures [1] can be used as ES hardeners.

Thus, insulating epoxy enamels elaborated for the resistors [46] containing a hardener in the form of dispersion in turpentine phthalic anhydride (20.0% turpentine). After curing at 160.0°C coating breakdown strength became 750 V (for a layer 0.1 mm thick).

There are some well-known epoxy compositions [47] for insulating coatings, which contain (wt %): 77.0 epicytols ES 828; 23.0 ES DUO22; methyltetrahydrophthalic anhydride 53.0; 35.0 metilendometilentetragidroftaleve anhydride; 0.1 salt of 2-ethyl-4-methylimidazole with the 2-ethylhexanoic acid. The composition is cured for 25 min at 140°C it has heat resistance and 108°C $\rho_v = 6 \cdot 10^2$ (ohm · cm)/100°C.

The author [48] developed an electrically insulating polymer composition destination consisting of bisphenol ES brand ED-20, oligoefiruretana terminated furan ring and MA as a hardener.

However, a large volatility, high toxicity and MA reactivity cause relatively low viability compounds and adhesives, and also increased the melting temperature of some other solid anhydrides (phthalic, trimellitic and D). they have some undesirable properties. In addition, solid anhydrides are poorly soluble in organic solvents and epoxy oligomers and they are commonly used in the manufacture of powder paints and lacquer compositions where they are used rarely.

From other anhydrides it is advisable to use trimellitic and pyromellitic anhydride, giving the cured materials of high thermal stability. In order to improve compatibility with the hardener varnish composition prepared from these anhydrides with glycols adducts. Adducts are gummy products that are readily soluble in organic solvents [36].

The development of liquid hardeners (methyltetrahydrophthalic, metilendikovogo and dodecyl anhydride) allowed to significantly expand the scope of the anhydride hardener type [36].

Curing terpene resins. Despite the fact that the scientific literature is insufficient data on the use of terpenoid resins (rosin, tall pitch, kanifolnomaleinovyh adduct (CMA), terpenomaleinovyh adduct (TMA) and kanifolnofumarovogo ad-

duct (CFA)) for curing the EC, thanks to its diverse valuable film-forming and physicochemical properties, they can be successfully used in the development of new formulations of thermosetting compositions.

For example, there are some sources that provides information [49] on the use of ES hardeners for diamine ethoxylated tall oil, which significantly improves the anticorrosion properties of coatings for metals.

According to the data [50] a method of obtaining a varnish composition, which consists in adding to the adduct ES MA is tall pitch. The adduct is prepared by heating a mixture of pitch and at AI 150–250°C. ES is preferably used with $M < 1000$.

We investigated the possibility of using AI and adducts of rosin resin acids [51] for the curing of varnish baking is based on ES. The resulting coatings have good mechanical properties and are resistant to corrosive agents. It is found that the dielectric properties better in coatings derived from low molecular ES.

A mixture of kanifolnofumarovyh adducts with ES in a solvent is the well known composition [52]. The coatings can be used to protect the metal, paper, wood and others.

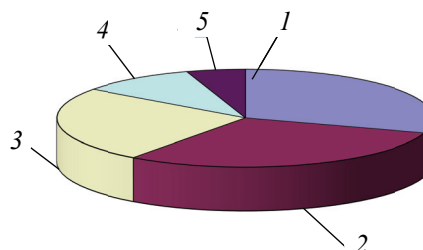
Thus, as can be seen from the survey, we developed a wide range of epoxy products for the electrical industry.

Graphical representation of a generalized group composition of thermosetting compositions shown in the Figure.

Depending on the used curing agents and ES thermosetting coating can be obtained with a wide range of physical, mechanical, electrical and adhesive properties.

In our opinion, these goals are the most promising TMS (or adducts TMA) resins.

Availability, high reactivity (presence of anhydride groups), low volatility, good film-forming properties, higher dielectric properties, solubility in many organic solvents, compatibility with ES, is good adhesion to many substrates, high heat resistance makes TMS resin very promising for use in thermosetting compositions .



Graphic image generalized group composition thermosetting compositions
1 – ES; 2 – hardener; 3 – solvent;
4 – softener; 5 – inorganic filler

It is used abroad, [53–57] and also has domestic application [58]. The authors developed methods for the preparation of TMS turpentine resins, in the presence of catalysts: salicylic acid, H_3PO_4 , iodine and H_2O respectively.

According to some studies [58], TMS resin is a multi-component systems, which are mono-alloy (α -adduct phellandrene, α -terpenes, 2,4-*n*-mentado and 3,8(9)-*n*-mentado) and diadduktov terpene hydrocarbons turpentine with AF.

Table 1 shows the quantitative composition and the physicochemical properties TMS resins produced by the process [57, 58].

Table 1
The quantitative composition and physical-chemical properties of therpenmaleic resins

TMS, obtained by the process	Mass fraction adduct, %		Physical-chemical characteristics	
	monoaddukt TMS	diaddukt TMS	T_s , °C	CN, mg KOH/g
[57]	85	15	45	314
[58]	40–43	57–60	65–70	320

As can be seen from Table 1, structure and physical-chemical properties of the resins are dependent on TMS catalyst in the presence of which interact with turpentine terpene hydrocarbons MA.

Thus, catalysts such as I_2 [57] and the diene synthesis shift reaction to obtain monoadduct.

At the same time a decrease in the softening temperature T_r and the acid number allow to obtain CN from the TMS resin. H_2O type catalyst shifts the reaction of diene synthesis to produce diadduktov with a corresponding increase in T_s and CN.

It is therefore evident that the compositions based on thermosetting resins such TMS obtained by the methods [57, 58] (because of the different composition of the group), will form a coating with different physical or mechanical properties that may hinder their subsequent use in electro industry. In addition, according to the literature, this question (the effect of TMS on the composition of the resin properties of the resulting thermoset coating) has not been studied.

Thus, the authors [53–56] provides compositions using TMA adduct obtained in the presence of a catalyst H_3PO_4 . Thermosetting compositions give coatings with that possessed low parameters: hardness, dielectric properties, adhesion to metals and mechanical strength. Therefore, they were not used in the electrical industry.

In order to eliminate these drawbacks by the authors [59–61] some formulations of thermoset-

ting compositions using the modified TMS (MTMS) resins have been studied and developed.

Table 2 shows the formulations of thermosetting compositions and mechanical properties of lacquers based on them.

Operational properties studied lacquer copper wire (diameter 0.5 mm, interval enameling 430/470 °C, enamelling speed of 20 m/min, coating thickness 0.04 mm).

Table 2
Preparation and physical-mechanical properties of lacquers

Composition thermosetting composition, wt %			Operational properties	
E-40	MTS	DBP	U_{br} , kV	σ , standard units
The paint obtained using the original TMS				
38	38	4	3.5	24
LA-6 (TMS, modified 1,5 wt % ZnO, $T_{reaction} = 190 \pm 5^\circ C$; $T_s = 70.0^\circ C$, CN = 310.0 mg KOH/g; partly it contains resinsates Zn) [60]				
38	38	4	4,0	60
LA-6G (TMS, modified 3.0 wt % zinc acetate and 4,0 wt % glycerol, $T_{reaction} = 190-220 \pm 5^\circ C$; $T_s = 82.0^\circ C$, CN = 160.0 mg KOH/g; partly it contains resinsates Zn and esters of glycerol) [61]				
54	22	4	6.1	100
GOST 21428–75			3.0	40

Note: The compounds listed thermosetting compositions without solvent.

As can be seen from Table 2, lacquers prepared using MTMS, by performance characteristics are higher than those lacquers that were prepared using the starting TMC. Lacquer LA-6 obtained using TMS depth with optimum chemical modification of 1.5 wt % ZnO have a high rate: breakdown voltage of 4.0 kV = U_{br} and mechanical strength (the number of double strokes of the needle) $\sigma = 60$ standard units.

LA-6G varnish was produced using TMS with optimum depth of chemical modification of 3.0 wt % zinc acetate and 4.0 wt % glycerol. It has the highest rates: $U_{br} = 6.1$ kV and $\sigma = 100$ standard units.

Tests have shown that the main indicators LA-6 and 6G lacquers significantly exceed the requirements of GOST 21428-75.

Therefore it is obvious that the very important area of research is the study of the effect of chemical modification of resins TMS on operational properties developed by thermosetting compositions.

It should also be noted that the actual impact studies are epoxy resins (of various molecular weights), characterized by the content of hydroxyl functional groups on the performance properties of thermosetting compositions.

Therefore it's important to create a new lacquer with a wide range of performance properties as appropriate:

- to investigate the effect of the quantitative and qualitative composition (mono and diadduktov) TMC on the physical-mechanical (dielectric, thermal stability, mechanical strength, adhesion) properties of the coatings;

- to develop high curing agents based on TMS resins, chemically modified nitrogen-, oxygen- and metal-containing compounds having a higher dielectric and physical-chemical properties, thermal stability, to improve the performance properties of lacquers;

- to establish a correlation: the molecular structure of ES – performance characteristics of copper coatings when cured developed hardeners;

- to establish a correlation between the chemical structure of the new terpenoid resins and performance properties of the resulting thermosetting varnishes;

- to develop a formulation technology and extend the scope of thermosetting varnish compositions.

Conclusion. As can be seen from the literature review, we developed a wide range of epoxy products for the electrical industry. Depending on the used epoxy resin curing agents and thermosetting coating can be obtained with a wide range of physical, mechanical, electrical and adhesive properties.

The most common curing agents are amines, epoxies, isocyanates, acid anhydrides and dicarboxylic acids.

Acids and their anhydrides can be presented as terpenoid class products. The presence in the Republic of Belarus of sufficient raw material base (domestic renewable terpenoid feedstock) for the production of rosin and turpentine, as well as the possibility of their processing into secondary products of JSC “Lesohimik” and other enterprises of the chemical profile of doing actual research to develop new effective terpenoid products and thermosetting compositions should be developed in the nearest future.

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