THE EFFECT OF THERMAL-RADIATION HEATING ON THE HARDENING OF EPOXY ENAMELS

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A presentation is offered with respect to the considerations governing the mechanisms of thermal-radiation activity on a film of an epoxy enamel applied to a compound ceramic backing.

Enamels based on epoxy resins have gained widespread acceptance in the radio-engineering and other branches of industry as efficient moisture-absorption coatings. The quality of the coating – extensively governing the operational reliability of all types of equipment – is determined primarily by the conditions of hardening for the sealing film. When convection drying is used to apply two coats of an epoxy enamel to a ceramic backing, the recommended hardening time is more than 5 h. This has a negative effect on the efficient planning of the applicable production process. In this connection, we have investigated a process for the thermal-radiation drying of ÉP-91 epoxy enamel on a ceramic backing, with our purpose being the determination of optimum conditions under which infrared radiation would affect the hardening kinetics and the quality of the resulting coating.

Investigations of green ÉP-91 epoxy enamel on an IKS-14 infrared spectrometer by a method described in [1] enabled us to determine the spectral optical characteristics of the film being dried, and these are shown in Figs. 1 and 2. We see from Fig. 1 (curve K_λ) that the enamel exhibits a characteristic transmission zone between 4 and 6 μ, while at the same time bands of significant attenuation of infrared radiation are observed in the shortwave region near $\lambda = 1\ \mu$, as well as in the longwave region, at about 8 and 12 μ, respectively. In other words, in the thermal-radiation range used in practical cases, as this applies to the coating under consideration, we observe relatively high absorption in the wavelength range whose maximum radiation corresponds to the working wavelength of light emitters.

In connection with the above, we should analyze the true nature of the absorption of the epoxy enamel, bearing in mind that the latter is applied to a calcined ceramic backing.

We know that the spectral absorptivity of the item fabricated from an enamel film applied to a backing can be determined [2] from the following:

$$A_\lambda^{\mathrm{ef}} = (1 - R_\lambda^{\mathrm{en}}) \left[1 - (1 - A_\lambda^{\mathrm{en}})^2 R_\lambda^{\mathrm{back}}\right]. \tag{1}$$

As follows from (1), the effective absorptivity (A_λ^{eff}) of the coating is a strong function of the spectral reflectivity (R_λ) of the backing surface. To determine the A_λ^{eff} of the compound material, we have processed the values of the spectral optical characteristics for the epoxy film according to (1), these characteristics having been taken from Fig. 2 at a number of appropriate points. Figure 1 shows the spectral curve A_λ^{eff} which characterizes the true absorption of the ÉP-91 enamel in the wavelength range of the infrared radiation of interest to us. In the calculations the spectral reflection factor for the backing over the entire investigated range was assumed to be approximately equal to $R_\lambda^{\mathrm{back}} = 0.5$. The latter was determined by analysis of literature data, from which it follows that for various types of ceramics (ceramics of thorium oxide, and alumina and magnesia ceramics) the values of the spectral reflectivity of their surfaces is found to vary between 55 and 64% [2, 3].

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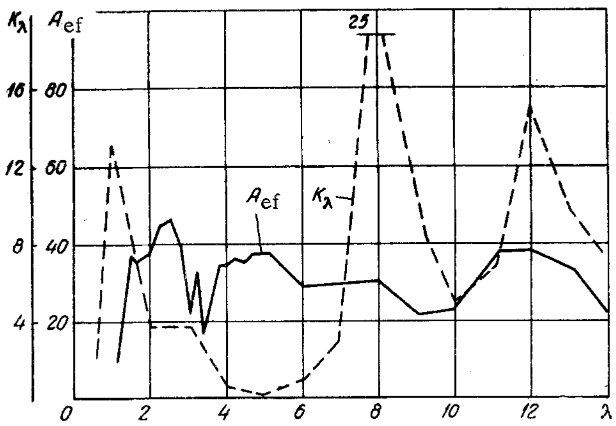

Fig. 1

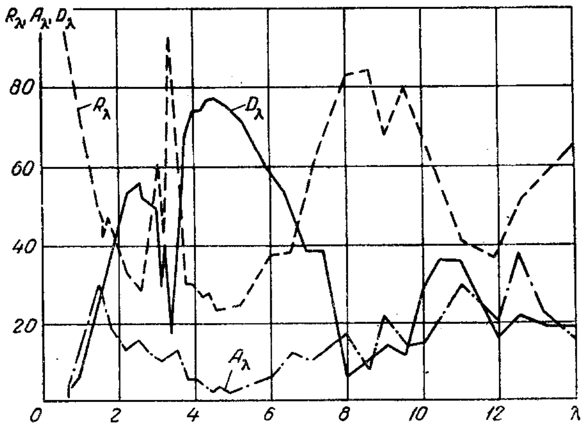

Fig. 2

Fig. 1. Extinction factor K_λ and effective absorption A_λ^{eff} as functions of the wavelength λ (μ) for ÉP-91 enamel.

Fig. 2. Absorption A_λ, transmission D_λ, and reflection R_λ as functions of the wavelength (μ) for ÉP-91 enamel.

An examination of the spectral curve for A_λ^{eff} shows that the compound material being studied here exhibits two characteristic regions of infrared-radiation absorption for λ = 1.2-2.0 μ and 3.8-6 μ, which is of practical significance from the standpoint of using appropriate radiant-energy generators for purposes of drying.

The green ÉP-91 enamel is a solution of É-41 epoxy resin, cresol–formaldehyde resin, and adipic acid in ethyl cellosolve with addition of pigments.

Mixtures of oligomeric epoxy and resol cresol–formaldehyde resins containing reactive epoxy, hydroxyl, and methylol groups require relatively high hardening temperatures. They combine as a result of the interaction between the methylol groups and, primarily, the hydroxyl groups of the cresol–formaldehyde resins and the epoxy groups of the epoxy resin. The active hydrogen atom attached to the molecule in this case inalterably goes to the oxygen atom of the epoxy group, thus forming a new hydroxyl group [5, 6].

We know that in the general case the primary effect of radiation on organic compounds involves the formation of free radicals. At the same time, the continuation of the subsequent processes depends on the point at which the free radicals originate as well as on the medium [4].

Thus in the case under consideration, for the effective conclusion of the cross-linking reaction for the epoxy enamel through the use of infrared radiation, it makes sense to expose the item to radiant energy, and this not only from the standpoint of developing adequate radiation densities to achieve the required film-heating temperatures; in addition, it makes sense to generate thermal radiation with a frequency close to the natural valence oscillations of the hydroxyl groups of the cresol–formaldehyde resin. This results in the most efficient absorption – from the standpoint of the kinetics of the process – of the thermal radiation by reactive groups as a result of an additional photochemical effect and the initiation of the process of forming the three-dimensional network of the polymer.

An examination of the infrared spectra of the complex molecules shows that the natural valence oscillations of the O–H group exhibit a rather broad frequency absorption band of 3700-2500 cm^{-1} [7]. According to the data of [7], for some epoxides in the overtone region at $\nu = 7042\ \mathrm{cm}^{-1}$ we also find absorption, whereas the longwave region with an oscillation frequency of 1250 cm^{-1} is the most characteristic for the epoxy group.

Comparison of the emission spectra of industrial infrared emitters with the indicated frequency range indicates the validity of employing KI 220/1000 light quartz emitters, as well as TÉN dark tubular emitters. This circumstance is a result of the distribution of their emission intensities over the spectrum in the frequency range (of interest to us) in which we observe rather high integral values for the radiant energy [2]. Here we should note that for the thermal-radiation drying of paint there presently exist no emitter designs capable of providing maximum radiation in the wavelength range λ ≈ 2.3-3.5 μ. Silit emitters or high-temperature gas emitters, because of their structural features, cannot be used in media containing solvent vapors.

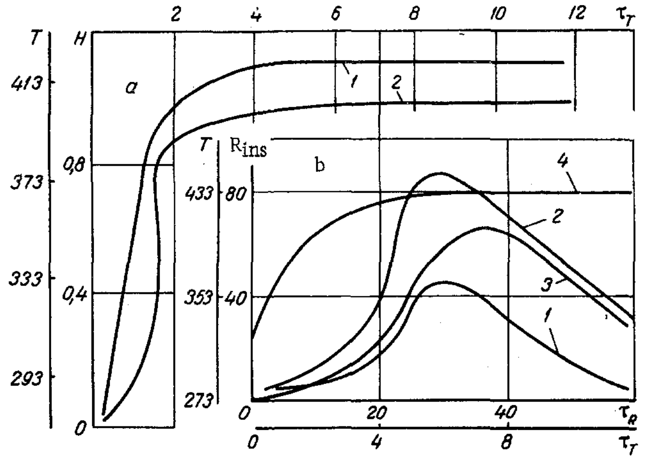

Fig. 3

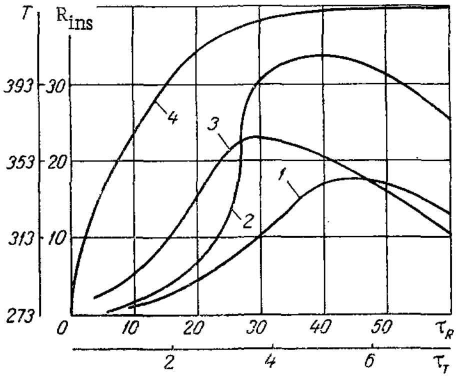

Fig. 4

Fig. 3. Change in the temperature T and in the hardness H for two layers of an enamel coating as a function of the time τ (min) in a chamber with light emitters (T, curve 1; H, curve 2): a) both the change in the insulation resistance R_{ins} and in the product temperature T as a function of the drying time for the second enamel layer; b) the drying time for the first enamel layer, respectively: 1) 20 min; 2) 10 min; 3) 3 min; 4) the change in the product temperature during the process of drying in the chamber with light emitters.

Fig. 4. Change in the insulation resistance R_{ins} and the product temperature T as a function of the drying time for the second enamel layer (the drying time for the first enamel layer is, respectively: 1) 20 min; 2) 10 min; 3) 3 min; 4) the change in the product temperature during the drying process in a chamber with dark emitters).

Thus it became necessary to investigate the kinetics and specific features involved in the hardening of an epoxy enamel under the action of both light and dark infrared radiation. The degree of hardening or cross-linking of the enamel film after drying can be evalued indirectly from the hardness of the coating and its resistance to both heat and moisture.

Under the conditions of the experiments performed here, the indicated controlled parameters were the relative film hardness H, determined with a pendulum device, and the insulation resistance R_{ins} (the airtight sealing of the protective coating), determined after the specimens were tested in a medium with $\varphi = 100\%$ and $T_1 = 313°K$.

Figure 3a shows the curves for the heating and the increase in the hardness of the epoxy coating in the case of thermal-radiation convection drying of the specimens with KI 220/1000 quartz emitters. As follows from the figure, within $\tau = 3$ min the hardness of the film reaches $H = 0.9$. According to the conditions under which the process is carried out, by this time the basic heating of the product is concluded and the product temperature has reached levels of $T_3 = 413°K$. The resulting hardness H of the sealing film is sufficiently high, since the known recommendations on these coatings work with a figure of $H = 0.8$; this indicates that the cross-linking of the coating has penetrated fairly deep.

The qualitative evaluation of the hardening kinetics for epoxy enamel on a ceramic backing was undertaken by the method of successively withdrawing identical test specimens from thermal-radiation chambers fitted out with light and dark infrared emitters which ensured identical integral conditions of thermal-radiation convection heating of the specimens.

The characteristic results of the experiments are presented in Figs. 3b and 4. As follows from the figures, in all regimes of thermal-radiation heating of epoxy enamels we observe extremal points (max), beyond which there is a pronounced drop in R_{ins}. This fundamentally important fact indicates that at a certain stage in the infrared radiation rather complete cross-linking of the molecules of the substance occurs during the process of hardening the epoxy film, and subsequent to this any further thermal radiation results in the undesirable effect of destroying the coating. Similar effects are noted when albumin is exposed to ultraviolet radiation [8]. Consequently, when an epoxy enamel is exposed for an unnecessarily long period of time to thermal-radiation drying the coating may begin to show signs of such undesirable phenomena of film destruction that in the final analysis it will become valueless as a sealing agent in products exposed to a moist atmosphere. This was precisely the situation found during the course of the control tests for R_{ins}. The experiments showed that it is possible to produce high-quality two-layer epoxy sealing coatings on a compound ceramic backing by means of thermal-radiation drying of the product with quartz emitters when $\tau \approx 50$ min and $q_{23} = 1.25$ W/cm^2, as opposed to the 5 h spent in actual practice.

Analysis of Figs. 3b and 4 also shows that the optimum values of R_{ins} – indicating the virtually complete cross-linking of the structure of the epoxy coating – appeared earlier when acted on by the light emitter which, in comparable time intervals, transmitted relatively more radiant energy than the dark generator, on a frequency corresponding to the natural valence oscillations of the hydroxyl group. As noted earlier, the most expedient approach in the case under consideration would be the use of emitters with a maximum radiation near $\lambda = 2.5$–$3.5\ \mu$, not only from the standpoint of efficient application of the radiation effect, but also in view of the need to reduce energy expenditures to the minimum in performing the drying operation.

It was also established during the experiment that the highest characteristics with respect to the quality of a two-layer coating were established in the thermal radiation of the first layer within $\tau = 10$ min. Here it developed that the attainment of relatively lower hardness and density for the epoxy film of the first layer ensures better adhesion of the second layer of the coating, and finally, provides for a denser structure of the two-layer of the protective enamel coating.

NOTATION

K_λ	is the coefficient of radiation attenuation in the Bouguer formula;
λ	is the wavelength;
A	is the absorption coefficient;
R	is the reflection factor;
T	is the temperature;
ν	is the oscillation frequency;
H	is the relative paint density;
φ	is the relative humidity of the air;
R_{ins}	is the insulation resistance;
τ	is the time;
q_{23}	is the density of the incident radiant flux.

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