

to which the reactive forms of glycidylamine are neutral, O-protonated and O,N-diprotonated ones. At $\text{pH} > 10$ the total reaction rate is determined by the rate of oxirane scission under the action of hydroxide-anions. Within the range $\sim 10 \sim 3$, O-protonated form is reactive. At pH lower ~ 3 reactive form of oxirane is O,N-diprotonated one.

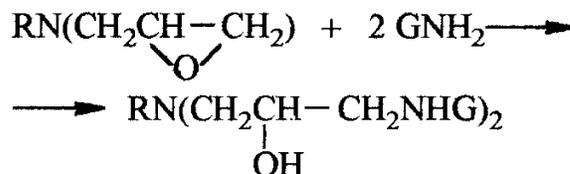
The results of kinetic studies make it possible not only predict the resistance of glycidylamines to hydrolysis but to calculate the rates of their reactions with nucleophilic reagents in aqueous solutions. In order to study the process of the reaction between oxirane compounds and gelatin which is known to proceed with amino and guanidine groups of this polymer, the kinetic investigations of the reactions in aqueous amine solution model system were carried out. Taken as model compounds were aliphatic amines having the basicity close to that of gelatin amino groups. With the excess of nucleophilic reagent its concentration remains practically constant in the course of the reaction and the product $k_{\text{NuH}} \cdot [\text{NuH}]$ is the first order rate constant which depends on the reactivity and concentration of the unprotonated amine form. The results of the kinetic studies of the reaction between glycidol and aqueous solution of morpholine reveal the increase of the reaction rate with the increase of pH . It is in the full agreement with the decrease in the degree of the amine protonation. This conclusion is confirmed by the data on the kinetic study of the reaction between triglycidylamine and aqueous solution of diethylamine. In the reaction of gelatin its basic groups are protonated depending on pH in the same way as amines. For this reason the rate of the reaction of oxirane compounds with gelatin increases with pH .

It has been observed that in neutral and slightly alkaline media diglycidylaniline reacts with gelatin much slower than diglycidylethanolamine, triglycidylamine and tetraglycidylhexamethylenediamine do. As pH increases the difference in reactivities decreases and at $\text{pH} > 10$ all four compounds react with gelatin at about the same rates. These dependencies, which are due to the differences in glycidylamine basicities with regard to oxygen atom, coincide completely with those observed during the hydrolysis.

Thus, it has been found that a di- (poly-) oxirane compound, when added to the gelatin solution as a hardener, is consumed for hydrolysis, which results in the lowering of its effective concentration. So it seemed important to determine the part of epoxide consumed effectively for gelatin hardening. The examination of the data obtained shows that this part increases with the increase in pH . While at high pH values ($\sim 9-10$) the effectiveness of hardener using is rather high (70-80%). In the media close to neutral it decreases considerably (to $\sim 10-20\%$). These conclusions have been made as applied to the condition studied (aqueous gelatin, 70°C). Under real conditions (room temperature, gelatin gel) the rate constants of epoxide reaction with both water and gelatin will be different, but the correlation of reactivities of oxiranes found from model experiments must remain the same.

Studying the Chemical Modification of Gelatin with Oxirane Compounds

In introducing oxirane compounds with two or more epoxy groups into gelatin emulsion layers cross-linked gelatin structures form, which results in changes in physicochemical, colloidochemical, membranous and photographic properties of photographic materials. The process of gelatin structuring with the participation of glycidylamines proceeds as a result of the reaction between the oxirane cycle and gelatin amino groups and can be represented by the following scheme:



In order to estimate the hardening action of the synthesized compounds, they were added to 3.5% solution of inert gelatin at pH 7 just before coating. The concentration range was $1.25 \cdot 10^{-5} - 2.00 \cdot 10^{-4}$ moles per 1 g of air-dried gelatin (ADG). Taken as criteria of the structurizing action of the compounds involved were melting temperature and mechanical strength of the swollen gelatin layer. The increase in the number of epoxy groups in the chemical modifier results in the intensification of its hardener action. Thus, tetraglycidylpolymethylenediamines are stronger structurizing agents as compared with triglycidylamine and the reactivity of the latter exceeds that of aliphatic diglycidylamines. With tetraglycidylpolymethylenediamines, the increase in hardening action with the number of methylene groups is observed, which quite agrees with reactivity and basicity of these compounds.

As for aliphatic diglycidylamines, there exists the relationship between the basicity and structurizing action. The experiments show that aromatic diglycidylamines have low reactivity and can only be used as structurizing modifiers together with hardening activators.

Hydrophilic-Hydrophobic Properties of Modified Gelatin Layers

Of great importance for the technology of gelatin emulsion layers is the optimization of their hydrophilic and hydrophobic properties. So it seems important to consider the relation between the hardener structure and hydrophilic and hydrophobic properties of modified gelatin layer.

The character of the gelatin layer surfaces was studied by determining the equilibrium wetting angle. As is evident from the experiments, the introduction of epoxy modifiers into the gelatin layer results, at room temperature, in the hydrophilization of the layer surface, which is accompanied by wetting angle diminishing as compared with unmodified gelatin. In the presence of nonstructurizing modifiers (e.g. monoepoxy compounds), warming up the gelatin layer does not influence the marginal wetting angle,

melting point and layer strength. The structurizing modification, which intensively goes on during the warming up the gelatin layer inclusive polyglycidyl hardener, is accompanied by noticeable increase in marginal wetting angle as compared with that for non treated material. This suggests a noticeable hydrophobization of gelatin layer surface in the hardening process.

Influence of Color Couplers on Hardening Process

Since the problem of the color coupler influence on the hardening process practically has not been studied, it seemed important to investigate the influence of both hydrophilic nondiffusing and protected color couplers on the chemical modification of gelatin layers by hardeners of glycidylamine series. The experiments were carried out using model gelatin layers, containing $5 \cdot 10^{-4}$ mol./g ADG of the several hydrophilic and protected couplers. Used as hardeners were glycidyl derivatives of aliphatic and aromatic monoamines as well as of alkylendiamines. The data obtained show that the presence of color couplers reduces the hardening process. Hydrophilic nondiffusing color couplers suppress the gelatin structurization to a greater extent as compared with the hydrophobic protected color couplers. The greatest effect is demonstrated by the yellow component of the blue-sensitive layer.

The measurements of hardener distribution between water and dibutylphthalate (DBPh) have shown that one of the most important factor in the case of protected color couplers is the capture of hardener by the hydrophobic phase of coupler dispersion and the corresponding reduction of its effective concentration in the gelatin layer. The results given in Table 3 show that the extent of tetraglycidylhexamethylendiamine extraction from the aqueous phase is noticeably higher than that of triglycidylamine. The higher the hardener concentration in the organic phase the greater part of it react with color coupler without taking part in gelatin hardening. Investigation of the structurization kinetics reveals that in the presence of protected couplers

dispersions the retardation of hardening with tetraglycidylhexamethylendiamine take place in much more extent than with triglycidylamine.

Table 3. Hardener extraction with DBPh from the aqueous solution

Hardener	Equilibrium concentration of hardener, mol/l·10 ³		$k_{\text{distr.}}$
	In water	In DBPh	
Triglycidylamine	10.4	5.40	0.529
	9.49	4.85	0.511
Tetraglycidylhexamethylendiamine	7.23	19.0	2.63
	5.28	15.3	2.90

Gelatin layers hardened in the presence of color couplers are characterized by the higher swelling ability as compared with the reference sample. This effect is more pronounced in case of nondiffusing color couplers.

Thus, it has been found that in the presence of hydrophilic nondiffusing and hydrophobic protected color couplers the hardening process becomes much more complicated. The influence of color couplers is different for different compounds of one and the same series. Hardening effect is determined by both the component nature and the hardener structure and properties. In case of using protected color couplers, the effectiveness of hardening depends, to a great extent, on the hardener distribution between the hydrophilic phase of the gelatin layer and the hydrophobic phase of color coupler dispersion.

Conclusion

A complex physico-chemical and technological study has been done aimed at the improvement of physico-mechanical and photographic properties of black-and-white and color photographic materials using oxirane modifiers.

A new class of chemical modifiers of gelatin emulsion layers – glycidylamines – has been studied.