

The Development of New Nucleating Agents for Fuji "INTEGRA" System

Kohzaburoh Yamada, Koji Kawato, Shigeo Hirano, Kazunobu Katoh
Fuji Photo Film Co., Ltd.
Minamiashigara Kanagawa 250-01 Japan

Abstract

The Fuji "INTEGRA" system in graphic arts has achieved extremely high image quality, high running stability, and the least amount of replenishment in the world through the development with a stable, amine-free processing solution having a pH of 10.5. One of the key technologies in this system is the development of two new nucleating agents, which are hydrazide compounds providing ultra-high contrast images by the well-known infectious development. One is for the scanner and camera films, and the other is the contact work films.

In the first place the high chemical reactivity of hydrazide compounds was strongly demanded in this kind of a low-pH developing system. And for this purpose the wide varieties of the acyl-groups in the hydrazide compounds were needed to examine in order to control pKa values of the hydrazides. The reduction of pKa values brought about higher reactivity, but at the same time it reduced the chemical storage-stability against the air-oxidation, so it was a difficult problem to satisfy both demands.

At this stage we invented a novel acyl-group that was designed for the intramolecular hydrogen bonding in a hydrazide compound, and it turned out to be a good solution to the problem.

For the contact work films, in which the absolutely low sensitive emulsion against nucleation is used because of the requirement for handling in an illuminated room, we made the most of the absorbable group onto a silver halide emulsion, such as a mercapto-containing heterocyclic group, and we also found out the best acyl-group in the hydrazide compounds providing the highest chemical reactivity in this low-pH system.

The purpose of this paper is to describe these inventions of new nucleators. Those were based upon studies of kinetic analysis of hydrazide compounds and studies of the correlation between photographic performances and structural demands.

Disadvantages of the trifluoroacetyl-hydrazide

The plausible reaction scheme of hydrazides is shown in Fig. 1. The active species of nucleation (diazene) is released through the first oxidation reaction between hydrazides and benzoquinone and the following hydrolysis reaction by alkali. High chemical reactivity in these processes is most important to get high nucleation activity even in the low-pH developing system. Especially the first oxidation reaction has to be fast, considering that it is a competitive reaction with sulfite. In the case of hydrazides having a sulfonamide linkage group, the reactive species in the oxidation process seem to be the di-anion of hydrazides, in which hydrazo-proton and sulfonamido-proton are both dissociated. (We call the pKa of hydrazo-proton pKa1, and the pKa of sulfonamido-proton pKa2 from now on.) So these two pKa values have to be reduced in accord with pH 10.5 of the processing solution to increase the rates of oxidation.

Trifluoroacetyl group(-COCF₃) is such a very strong electron-deficient group that it just seemed to meet the purpose. And it was also thought to be good for acceleration in the second hydrolysis reaction.

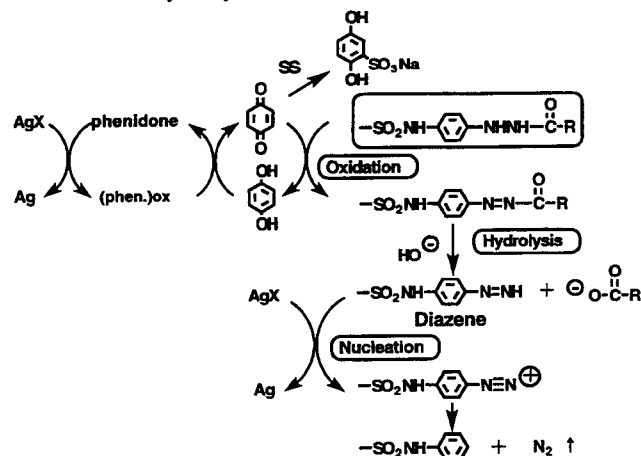
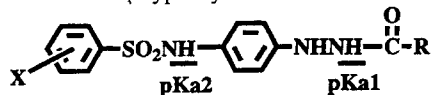


Figure 1. The Reaction Scheme of an Acylhydrazide Nucleator.

After all we were able to recognize its high nucleation activity in pH 10.5 processing solution expectedly,

comparing with -CHO type nucleators that had been used before. But at the same time the lack of chemical storage-stability was shown apparently in the compulsive test conditions. (Table 1) This was presumably because of its too low pKa1 value. That was to say, even when the trifluoroacetyl-hydrazide was just stored in the films, it was thought to be partially dissociated in the hydrazo-group, and to be oxidized in the air. Electron-deficiency of trifluoroacetyl group was apparently too strong for this system.

Table 1. pKa Values, Nucleation Activity, and Storage-Stability of the -COCF₃ Type Hydrazide.



-COR	pKa1*	pKa2*	Nucleation Activity in pH 10.5	Storage-Stability**
-CHO	12.0	9.8	Low	Good(95%)
-COCF ₃	7.71	10.55	High	Poor (42%)

*acetonitrile:H₂O=1:1, **residual amounts of hydrazides stored at 60°C, 65%, 3days.

Discovery of the novel acyl-group

Various kinds of acyl-groups in hydrazides were examined to find a moderate electron-deficient acyl-group between formyl (-CHO) and -COCF₃ group, that might satisfy both high nucleation activity and good storage stability for scanner and camera films. Actually the higher pKa1 exhibited the higher stability. But none of the hydrazides having enough storage-stability met the desired level of nucleation activity. It seemed that the reduction of electron-deficiency lowered the rates of hydrolysis and consequently nucleation activity. A strong electron-withdrawing group was recognized to be indispensable in the acyl-group for nucleation activity.

Our proposal to solve this conflicting problem stemmed from the fact that the intramolecular hydrogen bond between certain anionic group and certain hydrogen might increase the pKa value of it. We designed the following novel acyl-groups, as shown in Fig. 2, which had both strong electron-withdrawing groups and carboxylato groups in the same acyl-groups. The latter carboxylato group was expected to increase the pKa1 value by the intramolecular hydrogen bond with hydrazo-group, or at least by the neighboring effect of two anionic groups.

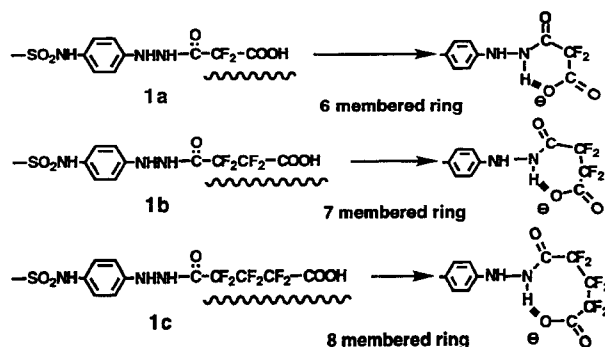


Figure 2. Molecular Designs.

2-Carboxy-tetrafluoropropanoyl hydrazide(1b) and 3-carboxy-hexafluorobutanoyl hydrazide (1c) were practically synthesized because their starting materials were easily available.

The results of experiments are summarized in Table 2. The pKa1 values of 1b and 1c were actually increased and their storage-stability were completely improved according to the increase of pKa1 values of them. In this case 7-member ring (1b) was better than 8-member ring (1c). Furthermore nucleation activity of 1b was found really a bit higher than that of trifluoroacetyl-hydrazide. (Fig. 3) "2-Carboxy-tetrafluoropropanoyl-group" has been proved to be the only acyl-group that fully achieved both good storage-stability and high nucleation activity.

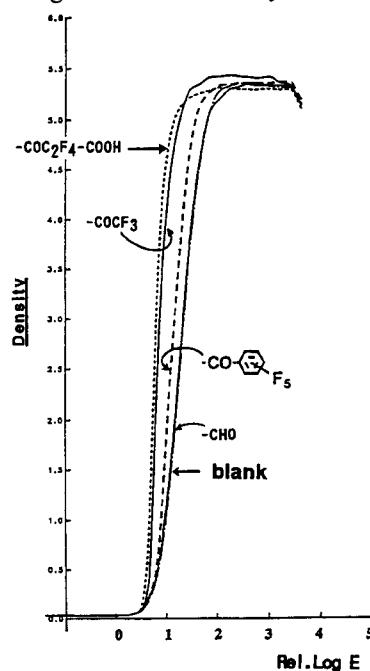
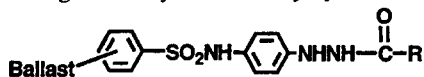


Figure 3. Sensitometric Curves of Some Acylhydrazides.

Table 2. pKa Values, Relative Kinetic Rates, Nucleation Activity, and Storage-Stability of Some Acylhydrazides.



Acyl Group	pKa1*	pKa2*	Oxid. rate**	Hydrolysis rate**	γ	stability %
-COCF ₃	7.71	10.55	1.00	1.000	17.1	42%
-COC ₂ F ₅	7.71	10.57	1.21	0.169	9.2	77%
-COC ₃ F ₇	7.70	10.09	0.98	0.080	8.3	79%
-COC ₂ F ₅ COOH	9.14	10.57	2.73	0.092	18.3	95%
-CO C ₆ F ₅	9.80	10.90	3.39	0.001	7.4	97%
-CHO	12.0	9.80	0.92	0.005	Low	95%

(*acetonitrile:H₂O=1:1, **acetonitrile:B.R.Buffer=1:1, pH10.5.)

Kinetic analysis of nucleation activity

For understanding the high nucleation activity of 1b above other ballasted acylhydrazides, the oxidation rates and the hydrolysis rates of various kinds of acylhydrazides were measured in an appropriate model condition. The results are shown in Table 2.

Surprisingly the hydrolysis rate of 1b was rather low, even though it had a strong electron-withdrawing acyl-group. This was presumably explained with the bulkiness of -COC₂F₅COO⁻ group, since the hydrolysis rates of another bigger acyl-groups than -COCF₃, such as -COC₂F₅, -COC₃F₇, and -COC₆F₅, were also low. (Table 2) But the reason why 1b had so high nucleation activity remained ambiguous. Here we started analytical approach to explain nucleation activity essentially.

First of all nucleation activity was conceived to have good correlation with the accumulated amount of diazenes for certain processing period. That amount was easily calculated through the following procedures.

- 1) The releasing rates of diazenes = $k_{ox} \times k_{oH}$
(k_{ox} = the rate of oxidation, k_{oH} = the rate of hydrolysis)
- 2) The total amount of released diazenes = $k_{ox} / (k_{ox} + k_{ss})$
(k_{ss} = the reaction rate of benzoquinone and sulfite)
- 3) The profiles of releasing diazenes were calculated from above-mentioned equations, as shown in Fig. 4.
- 4) The accumulated amount of diazenes for the processing period (30 sec) was obtained from these profiles.

The correlation between nucleation activity (γ ; contrast in sensitometric curves) and the accumulated amount of diazenes for processing period (30 sec) were shown in Fig. 5. Unexpectedly they were not in good correlation. Then the factor of hydrophilicity in hydrazides was taken into account in addition to the accumulated amount of

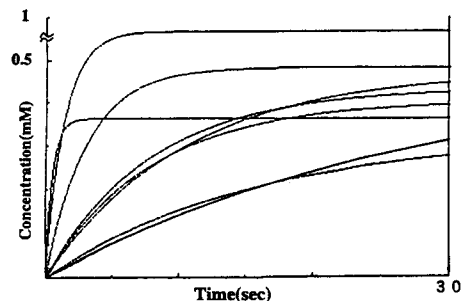
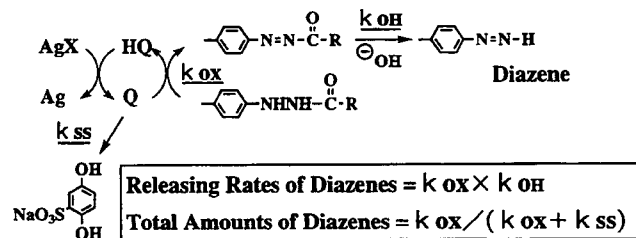


Figure 4. Generation Profiles of Diazenes.

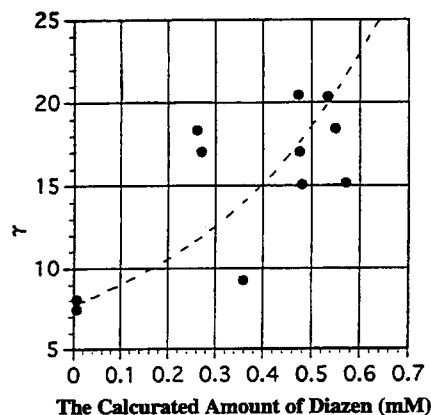


Figure 5. Relationship between Nucleation Activity and Amounts of Diazenes

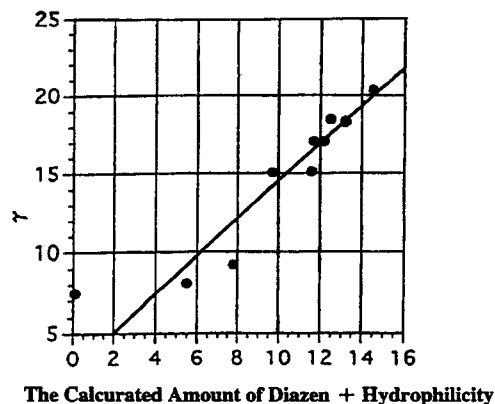


Figure 6. Relationship between Nucleation Activity, Calculated Amounts of Diazenes, and Hydrophilicity of Acylhydrazides.

diazenes, because hydrophilicity of hydrazides was supposed to affect practically their solubility, mobility, and diffusion in the films during development.

The results of regression analysis are shown in Fig. 6. Extremely good correlation between nucleation activity (γ) and these factors was found out. And accordingly the high nucleation activity of 1b was reasonably attributed to the hydrophilicity of its carboxylato group and its kinetic property in the release of diazene.

The most reactive acyl-group in hydrazides

As for contact work films, the highest level of nucleation activity was needed to conquer the wall of inefficiency for nucleation in low sensitive emulsion as mentioned previously. And for this reason -CHO type hydrazides having certain absorbable groups onto silver halide emulsion had been used. But this time we need more reactive nucleators suited for low-pH developing system.

First we applied the 2-carboxy-tetrafluoropropanoyl type hydrazide having 2-mercapto-5-tetrazolyl group as an absorbable group onto silver halide. (2c in Fig. 7) As an unexpected result, nucleation activity of 2c was not sufficient in this case. Supposedly the factor of hydrophilicity in its acyl-group didn't work well for this kind of hydrazides, because they were thought to exist in the surface of silver halide, and therefore to exist essentially in the hydrophilic environment. Then extra hydrophilicity in its acyl-group was probably helpless to improve nucleation activity any more.

We returned at the starting point to find the most reactive acyl-group in the chemical processes. Especially considering the rate of hydrolysis, less bulky acyl-groups, having suitable electron-deficiency at the same time, were examined thoroughly. And finally we found a certain acyl-group (2d). According to the kinetic analysis of it, it gave the fastest rates in both oxidation and hydrolysis reaction among all acylhydrazides, and therefore it gave the highest nucleation activity as shown in Fig. 8 and Table 3.

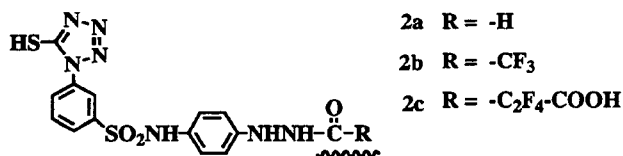


Figure 7. Some Acylhydrazides Having an Absorbable Groups onto Silver Halide Emulsion.

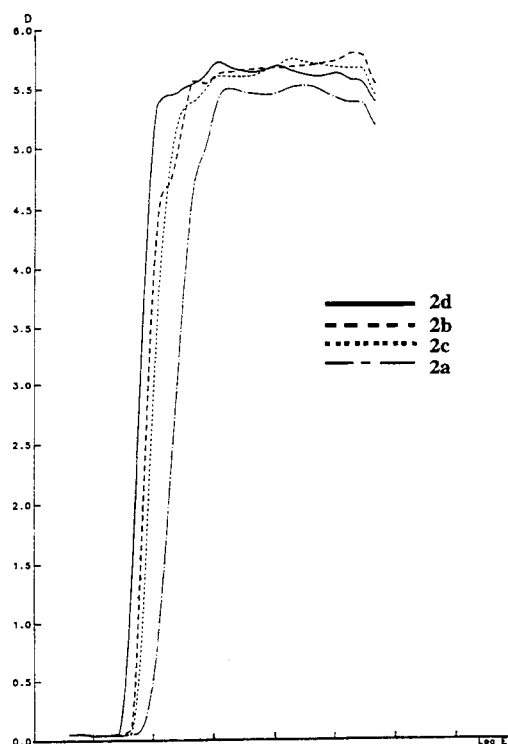


Figure 8. Sensitometric Curves of Some Acylhydrazides.

Table 3. pKa Values, Nucleation Activity, Storage-Stability, and Relative Kinetic Rates of Some Acylhydrazides.

No.	pKa1*	pKa2*	γ	Storage-Stability	Relative Oxid. Rate	Relative Hydro. Rate
2b	7.8	10.4	20.2	71%	1.00	1.00
2c	9.2	10.6	16.9	99%	1.24	0.11
2d	9.3	10.7	26.4	93%	1.64	2.29

(*acetonitrile:H₂O=1:1, Kinetic data were measured in acetonitrile:B.R.Buffer=1:1, pH10.5.)

References

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