A Fundamental Study on the Screenless Lithography

A View of the Mechanisms of Continuous Tone Reproduction

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The author approached the mechanisms of continuous tone reproduction in the screenless lithography from the side of sensitizing agents.

A commonly used o-quinone diazide compound was adapted as sensitizing agent, with which a grainless cleaned aluminum sheet was coated.

Effects of chemical and physical changes of the photosensitive coatings by UV rays irradiation on continuous tone reproduction were investigated by means of IR spectral analysis, wettability with water, profiling and micrographing the plate surfaces and densitometry of a printed color.

In order to eliminate any undesirable factor for the subject, smooth-faced grainless aluminum plates were used as the substrates.

The results are summarized as follows.

1) Ink receptivity and film thickness of photosensitive coatings after exposure and development decreased as the amount of exposure increased.

2) The structural changes of the coatings were micrographically observed as follows; cracks appear at first, then follows a network construction, spots remain dispersed and eventually these spots disappear from the plate as the amount of exposure increased.

1. INTRODUCTION

Screenless offset printing process, which is plate making lithographic plate from unscreened photographic film, has partly been put to practical use since it made its appearance on the U. S. market in 1965.

The mechanism of continuous tone reproduction in it remains yet unsolved. Up to date, the opinion[1,2] that the grain of aluminum support makes continuous tone reproducible is generally accepted.

In this study, we tried to make clear the mechanism of reproduction of continuous tone in screenless lithography taking notice on the changing in the form of photosensitive coating by UV irradiation time and eliminating effects of geometric surface form factor such as grains.

So far as we know, we do not have any report of studies pursued with ungraind supports. This is probably because the image resist strips off at the developing. we succeeded in settling it by using TAA sub-layer which 1 had devised[3].

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We used O-Quinone Diazide sensitizer which shows the peculiar photodecomposition reaction and then coated it on the grainless cleaned aluminum support having the TAA sub-layer.

We examined the mechanism of tone reproduction by IRRS, Wettability with water, density of inked up plate surface and print, profile, and SEM of the photosensitive coating after exposure and development.

2. EXPERIMENTAL

A. Materials and procedures

A smooth cleaned aluminum sheet (A 1050 P-H 18) material of 0.20 mm in thickness is coated with the following composition (Solution A).

Solution A

TAA*	10 ml
I. P. A	180 ml
CH_3COOH	1 ml
H_2O	30 ml

The plate is dried for 1 minute at 100°C and then heated for 1 minute at 250°C. The plate is coated with a positive working sensitizing solution (Solution B) and dried for 3 minutes at 100°C.

Solution B

Ortho quinon diazido sensitizer**	4 grams
Novolak phenol formaldehyde resin	1 gram
Methyl cellosolve	100 ml

Ortho quinon diazido sensitizer synthesised in the usual way. After drying, the printing plate thus produced was exposed to the light (fluolo lucent lamp, 1.25 mw/cm^2) for 15, 30, 45, 60 and 120 seconds. The exposed plate is then immersed in aqueous solution of 5% Na metasilicate for 1 minute at 22±1°C to remove the photodecomposition product. The developed plate is then washed with water, subsequently is treated with etch solution containing a small amount of phosphoric acid C. M. C, is allowed to dry at room temperature. It is then mounted on a offset printing press (RYOBIKR 2500), and inked up with greasy, black printing ink.

B. Mesurements

1. Mseurement of contact angle

Contact angles with water were measured at 15°C, 65% RH by using Goniometer to the printing plate, after exposing, developing and desensitizing respectively. The distilled water was used as the dropped solution (1 minute after dropping).

2. Mesurement of surface form and observation.

The roughness and form of plate surface were recorded with Kosaka Lab's Surface roughness Meter SE-3 C (needle type surface meter).

The plate surface was observed by using scanning electron microscope (SEM) and photomicroscopy.

3. Measurements of IRRS

Infrared reflectance spectra (IRRS) was recorded by using a Niphon bunko infrared Spectrometer Model IR-2 equipped with a PR-21 polarized reflectance apparatus.

4. Measurements of reflection density

The microdensity of printing plate both before and after developing and of print was

* TAA: Reaction product of tetra isopropyl titanate with acetylacetone in a molar ratio 1:1

** Sensitizer: Condensation products of a sulfonic acid halide of a naphtoquinone-1, 2-diazide and a novolak phenol formaldehyde resin

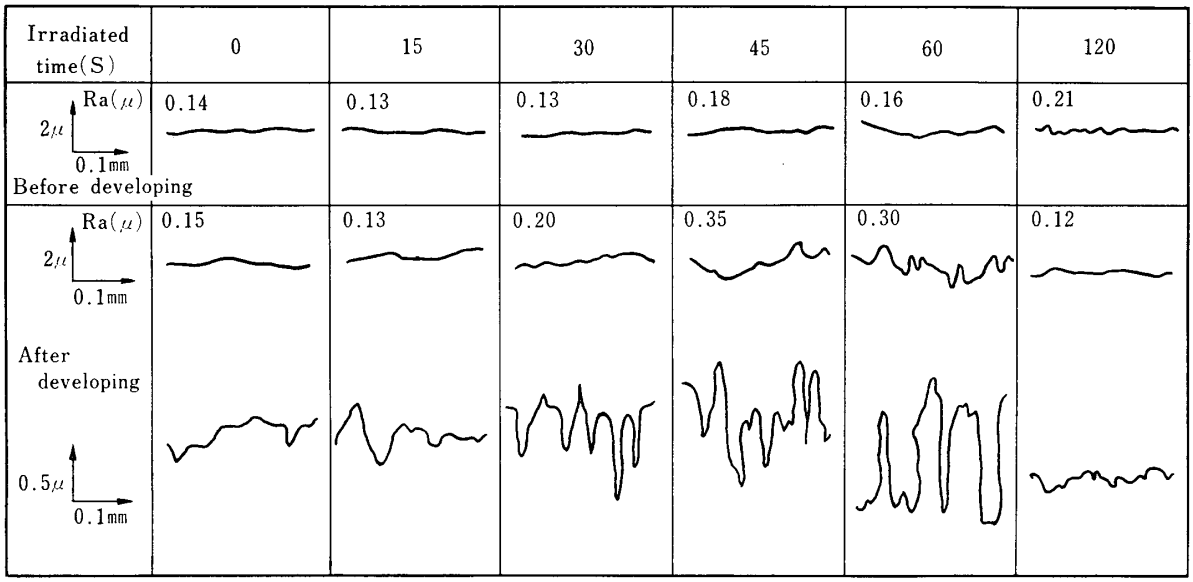

Fig. 1 Profile of photosensitive coating

recorded with SAKURA Microdensito Meter MODEL PDM-5 TYPE A. The reflection density of the inked up printing plate and of print were measured by using a Macbeth Densitometer RD-100 (A YELLOW filter).

5. Measurements of the amount of ink

The amount of ink on plate was determined by weighing the ink per unit area. The ink was allowed to dry at 100°C for 30 minutes.

3. RESULTS AND DISCUSSION

A. On the transformation of form of the photosensitive coatings by UV rays.

Film thickness and surface formation of photosensitive coating after exposure and development were recorded by Kosaka Lab's Surface Roughness Meter SE-3 C. From the profile of roughness curve of Fig. 1, the figure of photosensitive coating was observed to change according to the exposure time. These structural changes caused by the exposure time were recognized in the diazo photosensitive coating. As is clear from the following equation (Fig. 2), UV irradiation to the photosensitive coating caused the evolution of N_2 gas in it. The number and density of N_2 gas evolution increased in accordance with the exposure time (Fig. 3). After exposure this N_2 gas remained in the photosensitive coating in the form of gas bubble. In the completely unexposed photosensitive coating, N_2 gas evolution and the formal changes following it were recognized in the plate neither after nor

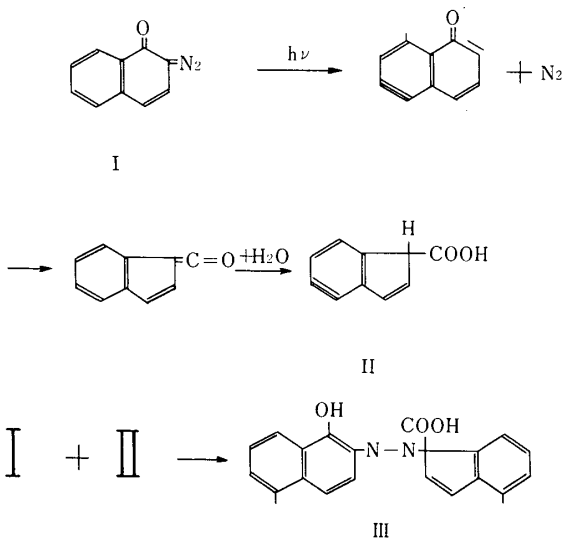

Fig. 2 Photochemical reactions of o-quinone diazide

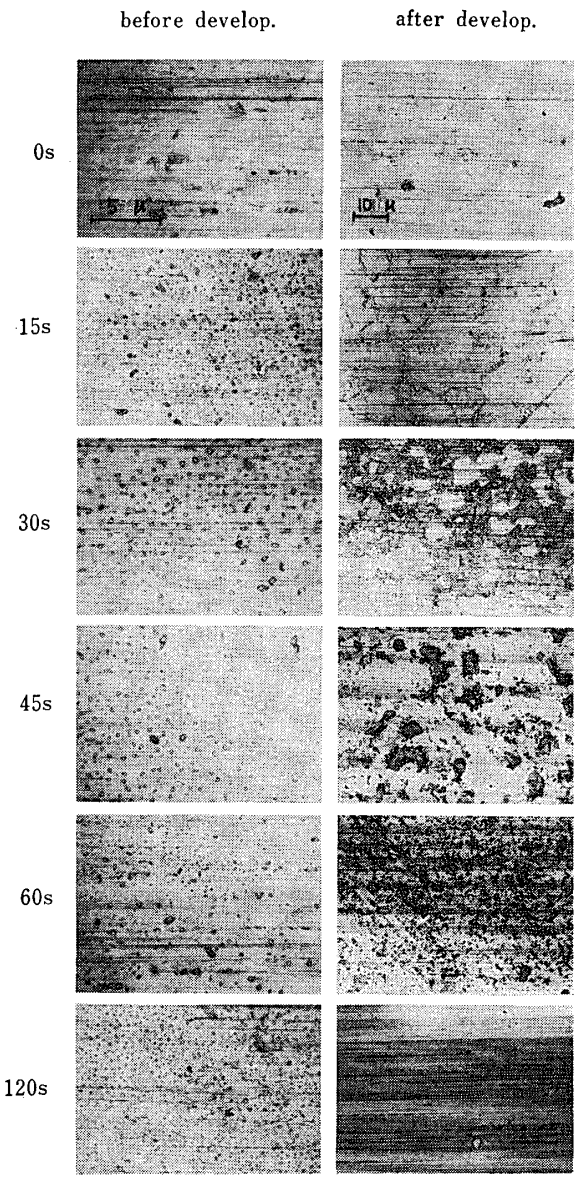

Fig. 3 Microscopic photographs of coating surface before and after development.

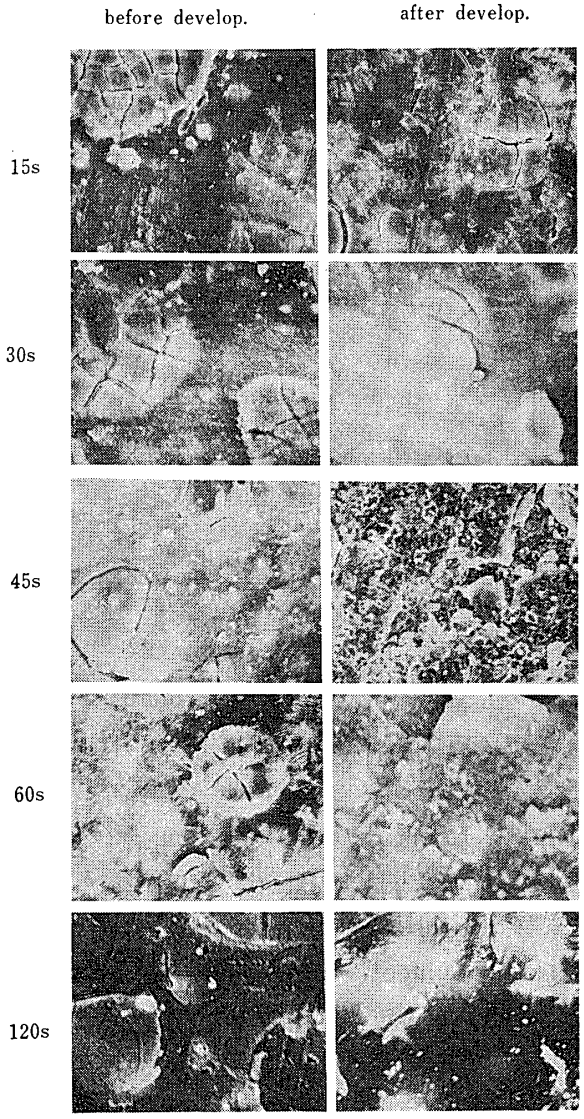

Fig. 4 Scanning electron micrographs of coating surface before and after development. (×1000)

before developing. The number of the evolution and the size of the bubble changed as the exposure increases (Fig. 4).

At the exposure time 15 sec, the size of the bubble was about 1 μm diameter, and with increasing of irradiation time, it grew enlarged. At the exposure time of 120 sec, the bubble evoluted also from around the bottom of photosensitive coating. The surface of photosensitive coating converted to an uneven one, which is due to the distribution of the gas revolution. After developing, the following transformation was recognized in the remainning layer according to the exposure time. At the exposure time of 15 seconds, after developing Ra of the remaining layer showed little change as compaired with one prior to the developing, but we recognized that some crack present in the photosensitive coating within 30 to 60 seconds of exposure time. Depending on exposure time, holes of differ-

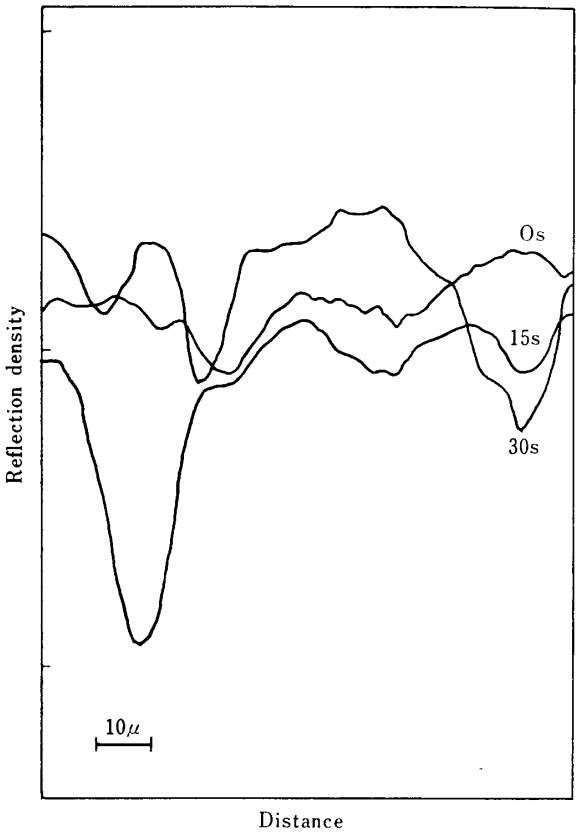

Fig. 5 a Scanning curves of coating surface after development.

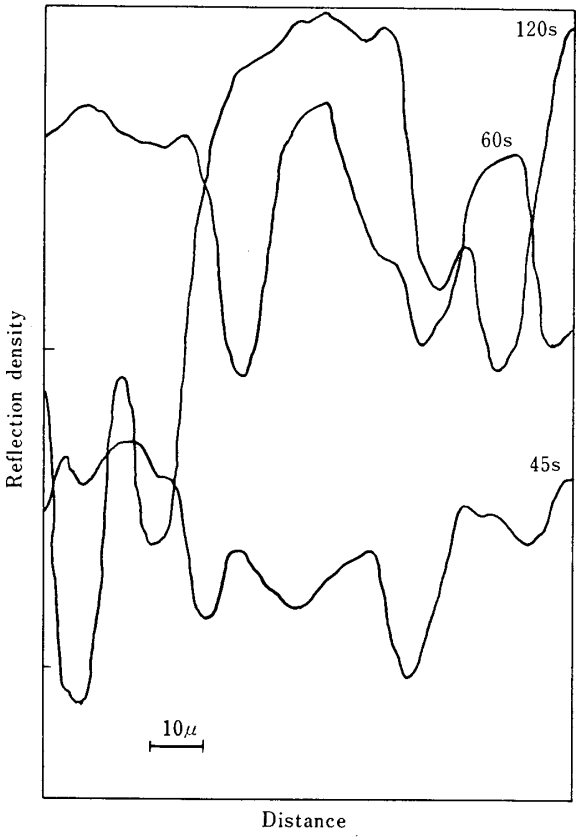

Fig. 5 b Scanning curves of coating surface after development.

ent sizes came out in it and took the form of a random dot construction. At the exposure time of 30 seconds, leaks sprang up in the remaining layer after developing. Their diameter varied from 50~200 μm. They had the shape of cone with their tops facing the base of cylindrical like needles.

The presence of N_2 gas bubbles plays a major role to accelerate the solubility of the decomposition product.

The photolytic compound was completely removed by the developing solution when it was fully exposed to irradiation for 120 sec. In this stage, the smooth TAA sub layer revealed itself and the resulting layer was not discerned. The value of Ra became smaller as compared with before development and approximated same to that of TAA sub-layer.

To sum up, the volume and distribution of the evoluted nitrogen gas changing gradually as exposure time increased were supposed to effect the solubility in development and caused the developed sensitive layer to have a random dot structure. The microdensity of the photosensitive layer after development was also determined by microdensitometer.

The results were shown in fig. 5. The density range of differences in distribution was enlarged as the exposure increased. We observed the same tendency in the results of roughness curve (Fig. 6).

We considered that the volume of photolytic compounds in the photosensitive coating, which was insoluble in developing solution, was

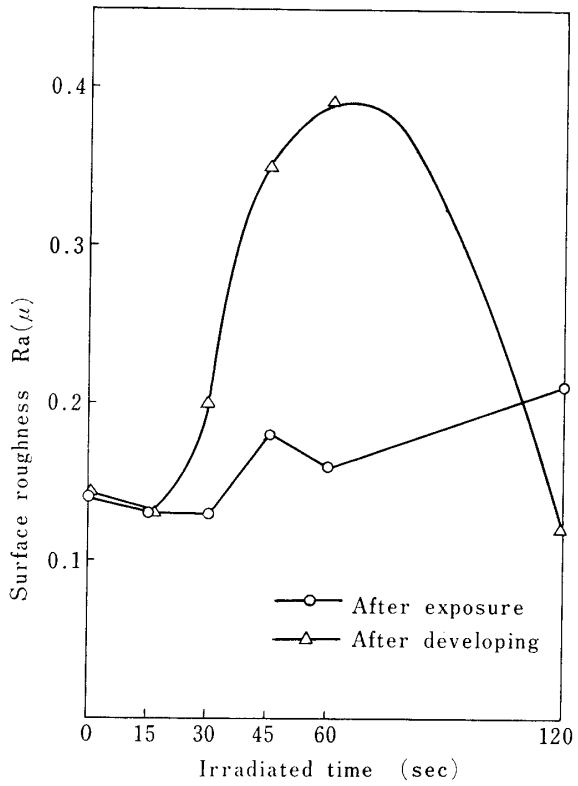

Fig. 6 Relation between the amount of exposure and surface roughness (average roughness) of the photosensitive coatings.

changed with the exposure time.

B. The relationship between ink receptivity and the amount of exposure

In fig. 7, the relationship between ink receptivity and the amount of exposure is shown.

The contact angle showed comparatively high value (θ : 65°) in the unexposed areas of the diazo sensitized layer and its value decreased as the amount of exposure increased. After the development, the exposed areas get more wettable with deionized water as the exposure increases.

Similarly, the ink adhesive weight on the remaining layer which was developed and desensitized decreased as the exposure increased (Fig. 8).

The structural formula of the unexposed o-quinone diazide is shown in fig. 2-I.

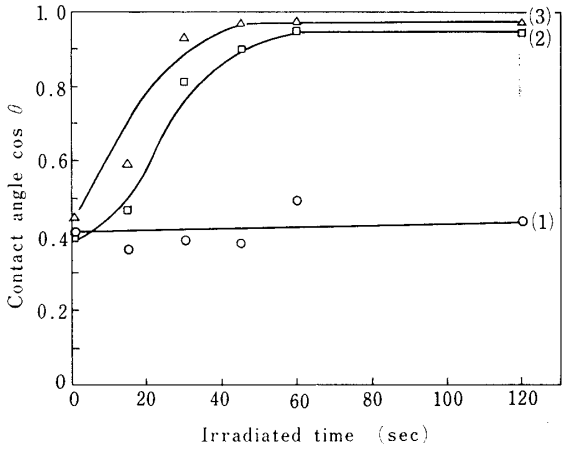

Fig. 7 Relation between the amount of exposure and wettability.
(1) After exposure
(2) After developing
(3) After desensitizing, rinsing, drying

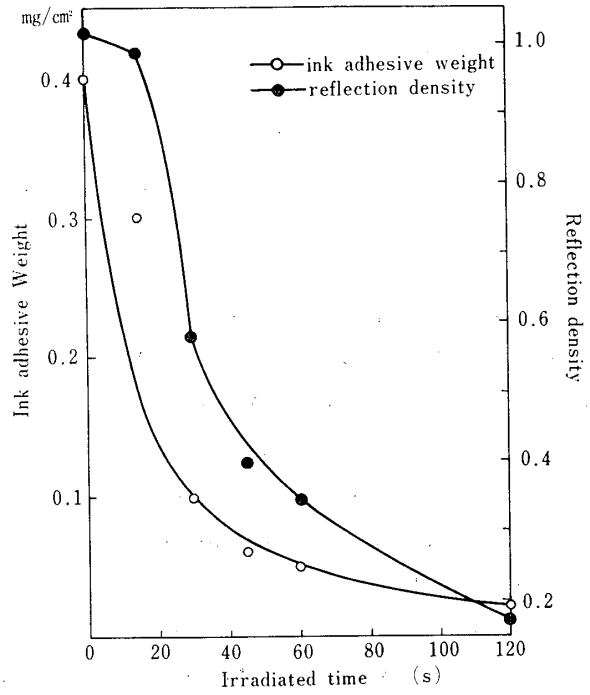

Fig. 8 Relation between the amount of exposure and ink adhesive weight.

It is oleophilic and its ink receptivity is good enough. Prints with maximum density value were taken from it using a conventional ink and press.

The fully exposed portion consists of completely photolytic diazo compound (Fig. 2-II),

novolak phenolic resin, and bubbles of N_2 gas.

It can be easily dissolved and removed in the alkaline solution, causing the surface of TAA sub layer to appear.

The value of its contact angle is below 20° and it is not ink receptive.

The density value of the non ink receptive part in the printed paper was found to be equal to the reflection density of paper.

Now, in order to reproduce continuous tone without screened photographic films, the ink receptive layer after processing needs to vary continuously with the amount of exposure.

This is thought to be similar to the conventional gravure type where the continuous tone seen on the press sheet is due to the thickness of attached ink. It may also be attained by changing of chemical construction. The change of wettability with the water is due to the change of molecular construction of the sensitized layer when exposed to ultraviolet light.

It is well known that the diazo compounds cause self coupling reaction in some range of exposure time in the presence of alkali and form the azo dye whose formula is considered as one in Fig. 2-III[4]. The coloring of violet during the alkali development proves this clearly.

Therefore we considered that the ink receptivity of photosensitive coating might depend on the quantity ratio of components I, II, III.

In order to confirm their chemical constructions, we measured infrared spectroscopy (IRRS) of the said sensitized layer on to the TAA sub layer, using a Japan Spectroscopic Infrared Spectrophotometer IR-2 (Polarized incident beem method).

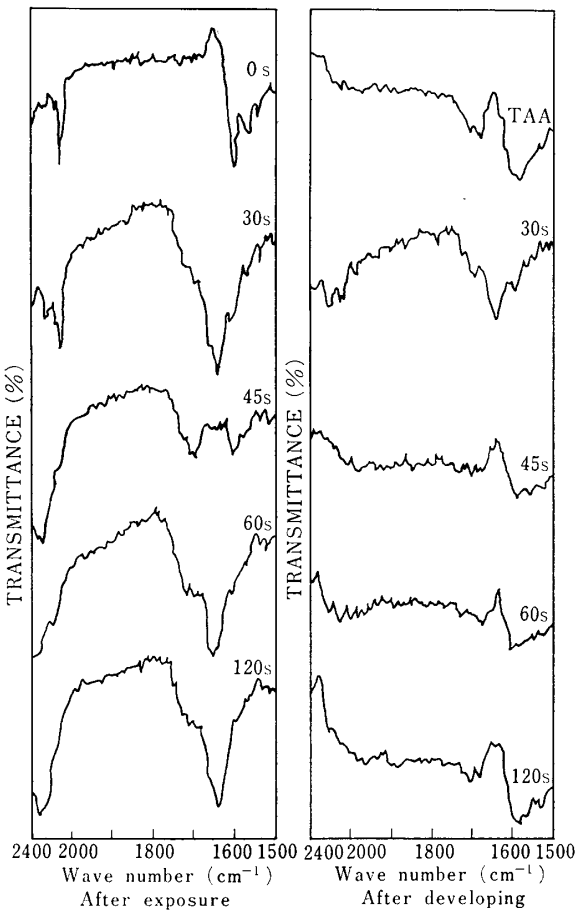

Fig. 9 Variation of IRRS of o-quinone diazide sensitized layer on the TAA sub layer after exposure and development.

Fig. 9 shows the IRRS of o-quinone diazide sensitized layer before and after exposure and development. As shown in fig. 9, the intensity of absorption bands of 2120, 1720, 1600 cm^{-1} changed by the irradiation of the ultraviolet rays. This fact means that, after the ultraviolet rays irradiation, absorption based on diazo radical of orthoquinone diazide of 2120 cm^{-1} which exists in the unexposed portion decreased with the increase of exposure time, and decomposition of diazo radical caused the evolution of N_2 gas. Simultaneously, absorption due to the indene ring appeared at 1720 cm^{-1}, which meant that indene carboxylic acid had been formed by the photodecomposition of

naphtoquinone diazide.

The absorption at 1600 cm^{-1} due to C=O of naphtoquinone diazide showed a remarkable decrease in its intensity by the light irradiation.

It was recognized that the IRRS of the remaining coating after development resembled to that of after exposure over the range of 0 to 30 seconds in exposure time. Over the exposure range from 45 to 120 seconds, IRRS of the remaining coating after development was similar to that of the TAA sub layer.

We consider that these IRRS show the condition of the plate after development. That is to say, they show us clearly the appearance of the image construction materials to which reproduce continuous tone.

4. CONCLUSION

Our experiments thus lead to the following conclusions.

The mechanism on the reproduction of continuous tone for alkalideveloped diazo-oxide resin sensitized unscreened positive working plate was explained as follows. After exposure and development, the film thickness of the diazo photosensitive coatings decreased as the exposure time increased. At the same time, the change of surface properties due to the change of the molecular structure was attested. That is; the alkali-developed diazo oxide resin sensitized coating got more wettable with water and ink receptivity decreased as the a amount of exposure increased. Furtl.ermore, physical structural changes were also observed in the coating in accordance with exposure time.

The volume and distribution of the evoluted nitrogen gas changing gradually as the exposure time increased were supposed to effect the solubility in development and to cause the developed sensitive layer to have a random dot structure. Therefore, the thickness of the remaining layer after developing, the size, depth and density of the holes changed as the amount of exposure increased.

The changes of dot area and the thickness of the remaining layer which formed the random dot images provided the continuous tone print. It could produce ink receptive spots that differed in area and ink thickness.

The multiple effects of change of ink receptivity owing to the chemical structural changes of the photosensitive coating corresponding to the amount of exposure and transformation of random dot structure in residual coating due to the distribution of the bubble of N_2 gas evoluted in the photosensitive coating after exposure contribute greatly to the reproduction of continuous tone in the photolysized type diazo-oxide resin sensitized unscreened positive working plate.

References

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