

Development of High Durability Cyan and Magenta Dyes for Ink Jet Printing System

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Abstract

Water-soluble novel cyan and magenta dyes, which show high ozone-fastness and light-fastness on porous photo media, have been developed for inkjet printing systems. Control of dye energy levels, removal of groups sensitive towards ozone, and acceleration of copper-phthalocyanine complex (CuPc) aggregation were the dominant factors to significantly improve both ozone-fastness and light-fastness. For the development of the CuPc cyan skeleton, alkyl sulfonyl groups, all of which were located at beta positions on the CuPc skeleton, were effective in improving dye fastness. For the development of the magenta skeleton, a combination of aniline-substituted pyridine coupling component and pyrazole diazonium component was an inherently important skeleton to improve dye fastness. Derived from the de-aggregation compounds developed for silver halide photography, we succeeded in developing an anti-bronzing ink additive.

1. Introduction

Color inkjet printers using water-soluble dye inks have now been widely prevalent to private households; and since January 2008, introduction to market of inkjet mini-laboratories using dye inks has begun first from US. The background of the popularization is that owing to the development of technology for print heads, inks and print media, prints of high quality and good fastness comparable to silver halide photographs have become obtained with ease. As the print media for producing image quality and feel comparable to those of silver halide photo prints, there are known porous papers prepared by coating resin-coated papers with porous silica or alumina fine particles, and swellable papers coated with a superabsorbent polymer; and porous papers having rapid drierability and high-speed printing aptitude and having excellent water resistance and glossiness are being the mainstream in the art¹⁾. We FUJIFILM have introduced porous-type photo papers into market as a brand "Kassai", and have received favorable comments.

However, up to now, there still exists a serious problem to be solved for more reliable use of porous-type photo papers by users. The problem is that the printed image is faded by ozone slightly existing in air within an unexpectedly short period of time; and since around 2000, the problem has been spotlighted by various media and its solution is greatly desired²⁾. In particular, cyan dye and magenta dye greatly fade, and magenta dye has another problem of poor light-fastness.

We report here the technical development of magenta and cyan dyes that have first broken the bar of inkjet color images to have high quality and good fastness comparable to those of the current silver halide photographs, essentially in point of the molecular design of those dyes capable of satisfying the properties necessary for use in inkjet inks and especially having greatly improved ozone-fastness.

2. Properties Necessary for Water-Soluble Dyes for Inkjet Printing Systems

The properties necessary for water-soluble dyes for inkjet

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printing systems are shown in Table 1. The color-relevant property and the image fastness greatly depend on the properties intrinsic to dyes; and therefore, needless-to-say, it is important to develop dyes capable of attaining these at a higher dimension. However, many other necessary properties are correlated with dyes, including, for example, printing density in which the dye existing condition on inkjet media significantly participates, prevention of bronzing that is often problematic in inkjet images, compatibility with various media, jetting reliability capable of jetting out ink droplets always stably and with good positional accuracy, ink storage stability, etc. Apart from these, there are still many other problems to be solved, such as the toxicity of dyes, the environmental compatibility and the production aptitude thereof.

Table 1 Demands for Good Image Quality.

	Necessary Performance	Necessary Physical Properties and Structures for Dyes
Color Property	Color Reproducibility	Light Absorption Characteristics (absorption maximum wavelength, half value width, extinction coefficient)
	Light Source Dependence	
	High Print Density	
	Bronzing Prevention	Mordanting Property, Solubility
Image Stability	Light-fastness	High Light-Fast Skeleton, Oxidation Potential
	Ozone-fastness	Oxidation Potential, Aggregatability, Low-Reactive Skeleton
	Water Resistance	Mordanting Property, Absorbability, Molecular Weight
	Moisture Resistance	
Ink Physical Properties	Jetting Stability	High Purity
	Ink Storage Stability	Solution Stability, Solubility, Antiseptic Property
Receiving Paper dependence	Difference Minimization of Image Color Properties and Storability	Solvatochromism, Mordanting Property
Production Aptitude	Raw Material Availability	Securement of Raw Material Availability
	Synthesis Aptitude	Special Reaction and Special Apparatus not required
	Cost	Inexpensive Material, Short Production Route, Production Process with High Yield and High Producibility
Material Safety	Absence of toxicity and Biototoxicity	Removal of Functional Group with High Physiological Activity, Control of Absorption and Accumulation Potential

3. High Weather Resistance Necessary for Inkjet Dyes

Fig. 1 graphically shows cross-section models of various imaging materials. A silver halide photo print has a UV absorbent-containing protective layer as the outermost surface thereof, by which almost all harmful UV rays are cut off. The hydrophobic dye imagewise formed in each photosensitive layer exists, along with the antifading agent therein, in the oil droplets emulsified and dispersed in a gelatin medium, and is protected from fading by light. Having the layer constitution, ozone penetration into the inside of the print is blocked, and therefore the silver halide photo print is almost free from a problem of ozonefading. In a sublimation-type thermal transfer photo print, the image surface is also covered with a thermal-transferred UV absorbent layer; and in this, the imagewise-transferred hydrophobic dye exists

inside the polymer matrix and is kept protected from ozone and UV rays. Different from these, in the porous-type inkjet photo paper excellent in ink absorbability, the printed water-soluble dye is kept in an extremely severe environment in which it is directly exposed to light, moisture, ozone, etc. In this case, it is difficult to make an antifading agent exist around the dye fixed on the silica or alumina surface, at a high concentration, and therefore, since the antifading capability could not be effectively functioned, the dye itself must be made to have high fastness. In particular, in the surface of the porous silica or alumina particles having a large surface area, the dye fading reaction by ozone is greatly accelerated, and therefore, it is the most important matter to develop dyes excellent in ozone-fastness.

On the other hand, regarding the fading of dye by light, there are known various decomposition paths; and in consideration of the above-mentioned environment of the inkjet image formed on a porous paper, it is anticipated that evading the fading path to occur in an oxidative atmosphere is important.

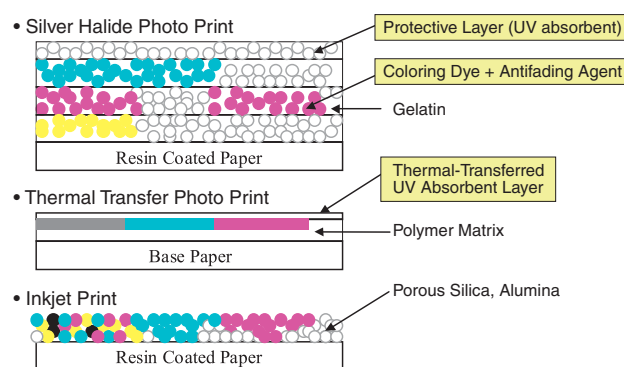


Fig. 1 Cross-section models of various imaging materials.

4. Development of High Durability Water-Soluble Dyes for Inkjet Printing System

4.1 Concept for Improving Ozone-Fastness, Light-Fastness

As in Table 2, it is known that ozone has considerably high electron affinity and oxidation potential as compared with oxygen³⁾, and can readily react with many organic compounds serving as a strong electrophile⁴⁾.

Table 2 Physical Parameters of Ozone and Oxygen.

	Ozone	Oxygen
Ionization Potential eV	12.30	12.07
Electron Affinity eV	1.92	0.15
Oxidation Potential (25°C) V	2.07	1.23

On the other hand, it is known that singlet oxygen that is one main factor of photo-oxidative fading of dyes is also a strong electrophile, and exhibits a reactivity similar to that of ozone⁵⁾. From the reactivity similarity between ozone and singlet oxygen it is expected that the molecular design for enhancement of ozone-fastness would be effective also for

enhancement of light-fastness.

The reaction of ozone with various dyes has been studied and reported in detail⁶⁾, and is widely utilized in industrial applications, for example, for decoloration of industrial wastes. However, there is not known any knowledge at all relating to dyes durable to high reactivity of ozone, and it is necessary to create the molecular design concept for high durability dyes. With the following three molecular design concepts, we succeeded in developing dyes of high fastness.

The first concept is to increase the oxidation potential of dyes. Concretely, an electron withdrawing group is introduced into the chromophore group, or the chromophore group is composed of a nitrogen-containing heterocyclic ring.

The second concept is to remove the substituent having high reactivity towards ozone. Concretely, the azo-hydrazone tautomerism of the azo group is fixed to the azo-form, or a dialkylamino group that is a common auxochrome group is removed.

The third concept is to utilize aggregation. Specifically, this is a concept of physically lowering the reactivity towards ozone by utilizing the aggregation potential of an organic dye of high flatness.

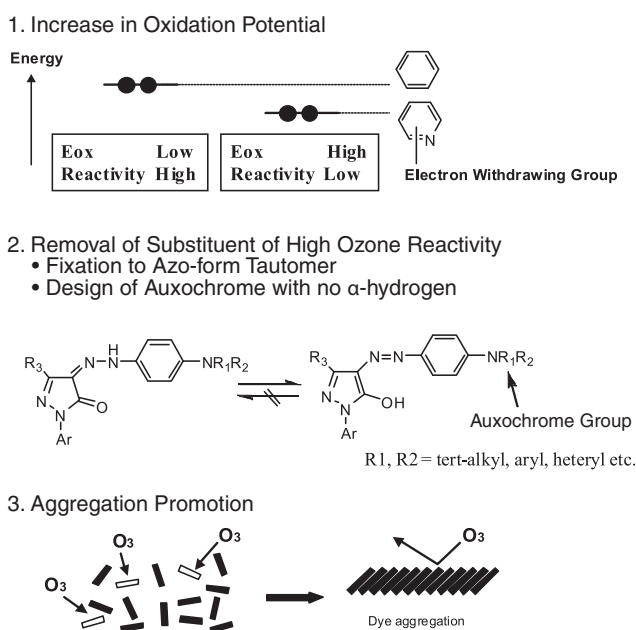


Fig. 2 Molecular design concepts of ozone-fast dyes.

4.2 Selection of Dye Skeleton

From typical dye skeletons, a copper phthalocyanine (CuPc) dye was selected for cyan and an azo dye for magenta, as the dye skeleton capable of accepting the above-mentioned

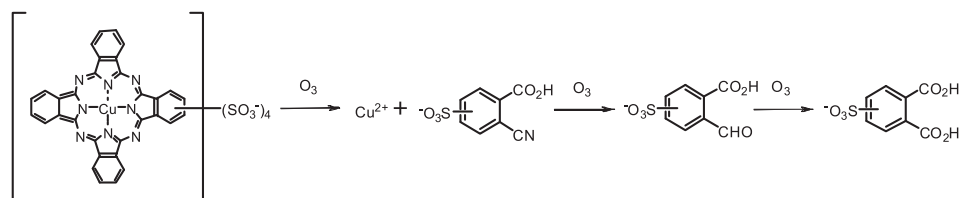
molecular design concept. The reason why a copper phthalocyanine dye is selected is because it has an extremely high light-fastness and is excellent in color hue and coloring power. In improvement of ozone-fastness, a molecular design was taken with the easily-aggregatable property intrinsic to copper phthalocyanine and the increase in the oxidation potential of the above-mentioned concepts.

Magenta dyes having various skeletons were used from the beginning, typically such as C.I. Acid Red 52 and the like azo dyes, all of which, however, were extremely unsatisfactory in point of both the ozone-fastness and the light-fastness⁷⁾. Nevertheless, we selected azo dyes, and the reason is because their basic color properties are good and the latitude in their molecular design is broad. As the policy for improvement of the ozone-fastness of magenta dyes, aggregation potential was not employed. This is because human eyes are extremely sensitive to the color hue in a magenta region, and when the aggregation state may change only a little depending on the receiving paper to be printed thereon, there may be a risk of clear recognition of the difference in the color hue between the printed papers. Accordingly, our policy is that, among the above-mentioned three molecular design concepts, the two of the improvement in oxidation potential and the removal of substituent highly reactive towards ozone are utilized to develop a novel dye skeleton.

4.3 Development of Cyan Dye

The cyan dye charged in the inkjet printer in the initial stage was almost a CuPc dye such as typically C.I. Direct Blue 87, 199. The ozone-fastness of these CuPc dyes is extremely poor. We analyzed the reaction between sulfonated copper phthalocyanine and ozone, and have known that the double bond between the carbon and the nitrogen constituting the macrocyclic π -electron unit is cut to give a phthalic acid derivative. W. E. Hills et al reported the same result, as in Scheme 1⁸⁾.

Investigating the above-mentioned reaction, we considered that the increase in the oxidation potential by introduction of a strong electron withdrawing group and the physical protection from ozone attack by formation of strong aggregation would be effective for the improvement of ozone-fastness. C.I. Direct Blue 87 and 199 heretofore popularly used in the art are produced through sulfonation of unsubstituted CuPc dye, but the regioselectivity in sulfonation of the starting dye is poor, and therefore, the product comprises a complicated mixture of dyes having a sulfo group randomly introduced into the benzene ring.



Scheme 1

For promoting the aggregation, the uniformity in the dye mixture and the molecular symmetry must be increased; and the position control of the substituent to be introduced is important. We synthesized CuPc dyes substituted with the same substituent only at the α -position and at the β -position, and compared them in point of the aggregation potential. As a result, we found that the β -substituted dyes have much higher aggregation potential. Further, we compared various β -substituted CuPc dyes in point of the ozone-fastness, and found that the electron-withdrawing property of the substituent on the benzene ring of CuPc and the ozone-fastness of the dyes have a relatively good correlation to each other, and therefore have known that, when an electron withdrawing group as strong as possible is introduced into the β -position to increase the oxidation potential, then the ozone-fastness of the resulting dye can be greatly enhanced (Fig. 3)⁹.

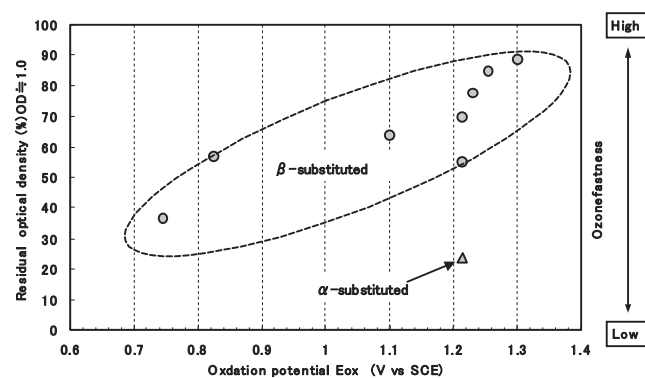


Fig. 3 Correlation between ozone-fastness and oxidation potential.

Regarding the selection of the electron withdrawing group to be introduced, the candidate is a sulfonyl group or a sulfamoyl group because of the necessity of introducing a water-soluble group into the dye. For attaining the same level of ozone-fastness with a sulfamoyl group having a weaker electron-withdrawing property as that with a sulfonyl group, the aggregation potential of the sulfamoyl group will have to be increased more than that of the sulfonyl group; however, since the problem of bronzing that is the bar to aggregation promotion as mentioned below may increase, we selected the sulfonyl group. On the other hand, in consideration of the latitude in formulating the inkjet ink and the stability security in production and storage of the ink, the solubility of the dye not precipitating under any service condition must be secured, and therefore, the water solubility of the dye is desired to be as high as possible. This is contradictory to increasing the aggregation potential. We further investigated these requirements and the data of the dyes, and as a result, have reached a cyan dye C-1 in which one alkylsulfonyl group is introduced into the β -position of all the four benzene rings to thereby increase the oxidation potential and to promote the aggregation, and the substituent on the alkylsulfonyl group is optimized. In C-1, a hydroxyl group is introduced into the side branch for further promoting the aggregation, and on the

other hand, a sulfo group is also introduced for securing the solubility of the dye in water, and in addition, an asymmetric carbon is introduced to give a racemic mixture. In that manner, the dye secures a sufficient solubility for practical use thereof as an inkjet dye. Fig. 4 shows the molecular structure of the developed CuPc dye C-1 and the molecular design concept for it.

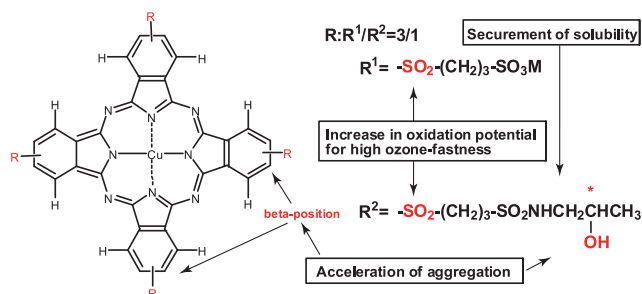


Fig. 4 Molecular design of high durability cyan dye C-1.

Fig. 5 shows the fastness data of the high-durability CuPc dye C-1 we developed. The ozone-fastness was about 30 times that of the ink A commercially sold at that time, under the condition of an ozone concentration of 0.5 ppm, and the light-fastness was enhanced by about 5 times as expected¹⁰.

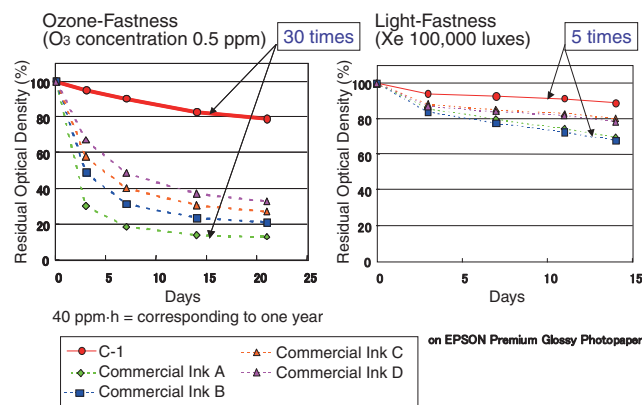
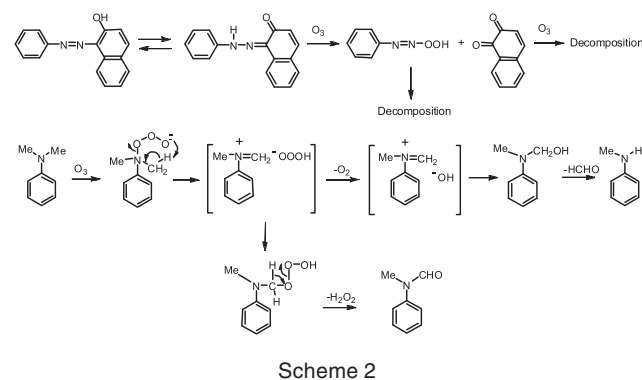


Fig. 5 Comparison of ozone-fastness and light-fastness of cyan dye C-1 with conventional dyes.

4.4 Development of Magenta Dye

It is well known that, in azo dyes, there exists azo-hydrazone tautomerism as in Scheme 2. In this connection,



Scheme 2

it is known that the hydrazone form mainly react with ozone and is thereby decomposed⁶⁾, in case where hydrogen atom (α -hydrogen) exists on the carbon atom adjacent to the nitrogen atom of the amino group of an auxochrome group, ozone electrophilically bonds to the lone electron pair on the nitrogen atom and subsequently the dye decomposes through the intramolecular α -hydrogen-drawing reaction. Accordingly, we made our development policy to attain the molecular design of only the azo form as the tautomer and to utilize the auxochrome group with no α -hydrogen.

Fig. 6 shows the molecular structure of the high-durability magenta dye we developed, and the molecular design concept for it.

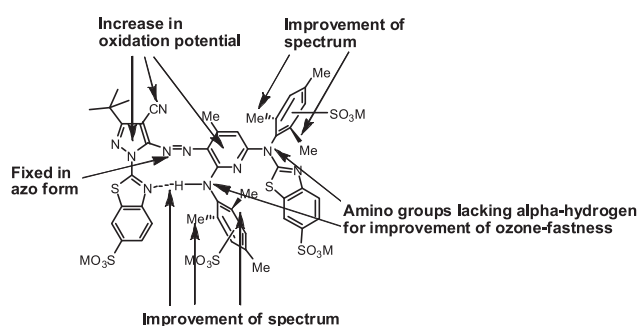


Fig. 6 Molecular design of high durability magenta dye M-1.

First, for increasing the oxidation potential of the dye, we specifically noted the azo dye skeleton comprising the heterocyclic diazo component and the heterocyclic coupling component, and investigated them. As a result, we have found that the azo dye composed of a pyridine derivative as the coupling component and a pyrazole ring with the 4-position substituted with a cyano group as the diazo component has high ozone-fastness and light-fastness. Further, we have found that introduction of an anilino group not having a hydrogen atom at the α -position into the coupling component to be an auxochrome group, and introduction of a benzothiazole ring to both the diazo component and the coupling component are the molecular design effective for satisfying both wavelength prolongation of the dye and ozone-fastness thereof. However, these were still unsatisfactory for producing a sharp magenta color hue having a narrow half value width of the spectrum. Regarding the improvement of the color hue, we considered that the benzene rings of the two anilino groups introduced into the coupling component are made to be vertical to the plane of the dye conjugated unit and the rotation of the benzene rings is restricted, and these may be effective for the intended improvement; and as a result, we introduced a methyl group into both the 2- and 6-ortho positions of the benzene ring, and have succeeded in constructing a magenta dye M-1 of which the color hue is nearly the same level as that of a magenta dye M-2 that was a typical dye at that time¹¹⁾. We further investigated M-1 in point of the type and the number of the water-soluble groups

relative to the solubility of the dye in ink, and have secured a sufficient solubility of the dye with no problem in practical use thereof as an inkjet dye, by introducing four sulfo groups thereto. We have confirmed that the oxidation potential of the dye M-2 is 0.61 V (to SCE), while M-1 has an extremely high oxidation potential of 1.38 V.

Fig. 7 shows weather resistance test results of the high-durability magenta dye M-1 we developed this time. As compared with the dyes M-2 and M-3 that were popular at that time, the ozone-fastness of the dye M-1 was about 10 times and the light-fastness thereof was about 6 times the conventional dyes.

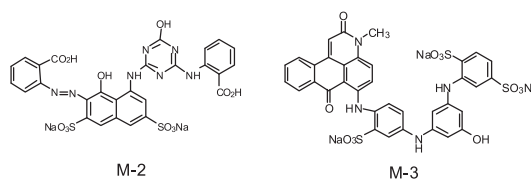
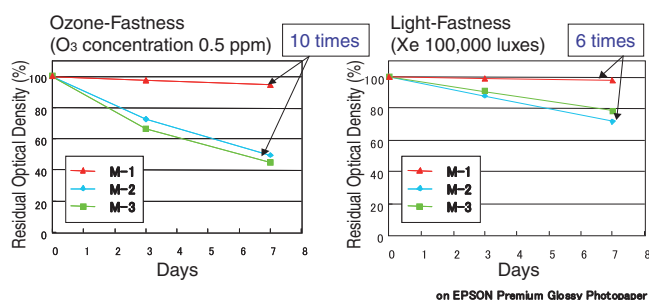


Fig. 7 Comparison of ozone-fastness and light-fastness of magenta dye M-1 with conventional dyes.

5. Development of Anti-Bronzing Technology

According to the molecular design described in the Chapter 4, we developed the dyes excellent in light-fastness and ozone-fastness; however, in practical use of the cyan dye, the problem that is contradictory to the aggregation potential of the dye has become noticeable in that the bronzing often occurs in the high cyan density part in the image with the increase in the aggregation potential of the dye. The bronzing is a well known phenomenon especially in use of pigment inks, and this phenomenon is that the light of a wavelength to be naturally absorbed is seen as a reflected light, and cyan dye gives a reddish violet reflected light. Regarding the bronzing occurring mechanism, there are some theories. One is that the crystal structure and the refractive index of pigment may participate therein, and another is that the phenomenon will be caused by the selective reflection on the particle layer formed on the surface and comprising particles having irregular sizes; however, the mechanism is as yet unclarified¹²⁾. Dyes having a higher aggregation potential or those having a lower solubility may tend to give bronzing, but the dependency on the receiving paper is also great.

The left side of Fig. 8 is a microscopic photo showing a

bronzing. From the left lower photo piece, it is known that the dye did not almost penetrate but existed as concentrated in the limited surface of the medium. Probably, it is considered that large dye aggregates would be formed and the penetration would be thereby retarded, and the localization of the dye in the medium surface would be promoted. Accordingly, we investigated an additive for controlling the size of the aggregates. An aggregation controller for sensitizing dye, which had been developed in the technology of silver halide photos, was added to the ink, whereby the bronzing was significantly retarded, as in the right-side photo in Fig. 8. It is known that, owing to the effect of the aggregation inhibitor, the dye penetration was promoted, as in the right lower photo. In addition, the ink viscosity was lowered. The aggregation controlling technology which we employed this time is a technology for promoting the disaggregation of sensitizing dye by the additive having a strong interaction with sensitizing dye for the purpose of removing color staining after development that is derived from the sensitizing dye in a J-aggregate state existing on silver halide particles. By retarding the aggregation, there may be a risk of deterioration in ozone-fastness; but in fact, the ozone-fastness was bettered on the contrary. Though not clarified, the reason why the ozone-fastness was bettered may be considered because the number of aggregated dyes could be reduced in some degree but they could not have any significant influence on the fastness of the aggregates and the additive would react with ozone in place of dye.

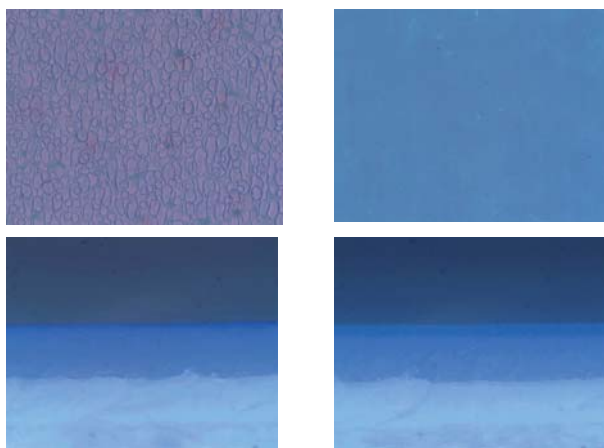


Fig. 8 Effect of anti-bronzing ink additive.

6. Establishment of Production Method for High-Purity Dye with Ink Aptitude

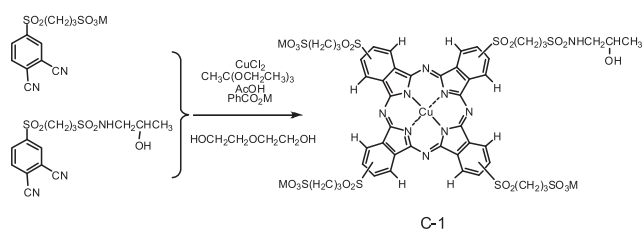
As described in the above, we developed dyes having a greatly improved fastness, but for using them in producing inkjet inks, there was still a problem relating to the quality of the dyes specific to inkjet printing systems. Here at the end, we describe this briefly. Regarding the technology of dye production, comprehensive papers were presented in the Journal of the Association of Organic Synthetic Chemistry,

Vol. 67, No. 1, and are referred to herein.

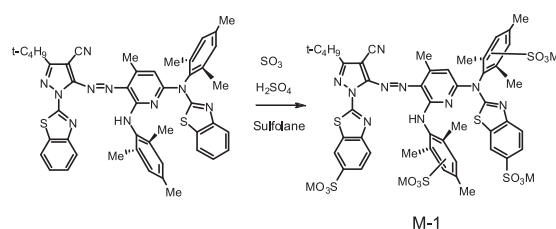
For securing the jetting stability of fine liquid droplets of ink to be jetted out from a print head and securing the ink storage stability, the inkjet dyes are required to have high purity and stable quality. Accordingly, establishment of synthesis technology that secures high purity and repetitive reproducibility is the point for quality stabilization. Those to which special attention should be paid are polyvalent metal ions and salts that are said to be a cause of clogging of ink heads.

In cyan dyes, all the substituents introduced into the benzene rings of the CuPc skeleton must be β -positioned. For these, therefore, a production process is employed in which a phthalonitrile derivative having necessary substituents previously introduced thereto is prepared, and this is cyclized in the presence of a copper ion in the final step to give a CuPc dye (Scheme 3); and accordingly, it is important to minimize the free copper ion content in the final product of dye. Regarding this, the cyclization reaction was investigated in detail and the condition under which the reaction could go on quantitatively was found out; and by optimization of the dye isolation condition and by the severe quality control, stable production of dyes was secured.

The magenta dye M-1 is produced by constructing the basic skeleton that comprises four nitrogen-containing heterocyclic rings and two benzene rings, followed by sulfonation in the final step. In the sulfonation step, for maintaining the desired color hue and the high durability at a constant quality, a sulfo group must be regioselectively introduced into the two benzene rings and into the two benzothiazole rings, totaling in 4 positions (Scheme 4). The dye must be isolated from the reaction liquid where a large excessive amount of a sulfate salt exists therein, and the quality of the product dye must be stabilized as the final product of high purity. We investigated various sulfonation conditions and enabled regioselective sulfonation under a



Scheme 3



Scheme 4

mild condition by using anhydrous sulfolane as the solvent and using sulfur trioxide as the sulfonating reagent. Using sulfur trioxide makes it possible to minimize the sulfate salt to be produced in the reaction. Next, we investigated the method for isolation of the formed dye and established the purification method using a separation membrane, thereby completing the industrial production in which the amount of the remaining sulfate ions is minimized.

7. Conclusion

We developed cyan dye and magenta dye excellent in light-fastness, ink jetting stability and storage stability. These dyes were exponentially improved in fading resistance to ozone gas of inkjet color prints that has been problematic recently in inkjet printing on porous-type inkjet photo papers. Fig. 9 shows print samples with inks with cyan dye C-1 and magenta dye M-1, and print samples with conventional inks, indicating the ozone-fastness of those samples as compared with each other (corresponding to forced ozone-fastness test for 3 months). In addition, we developed the technology of an additive capable of reducing bronzing.

The points of the development are as follows:

- 1) The mechanism of ozone fading of dyes was analyzed, and three concepts for reducing the reactivity towards ozone were completed. The concepts are the increase in oxidation potential; the removal of substituent having high reactivity towards ozone; and the aggregation promotion. According to the molecular design based on these concepts, we succeeded in constructing a new cyan dye and a new magenta dye. The cyan dye attained 30-time ozone-fastness increase, and 5-time light-fastness increase; and the magenta dye attained 10-time ozone-fastness increase, and 6-time light-fastness increase.
- 2) The bronzing that is the adverse effect of utilizing the dye aggregation potential was reduced by the aggregation controlling technology we cultivated in the field of silver halide photography.
- 3) We realized the production method and the purification method excellent in repetitive reproducibility, in which the content of polyvalent metal ions in the dye to be a cause of clogging of inkjet heads can be minimized.

The above-mentioned molecular design concepts have good versatility, and we applied them to development of high-durability yellow dyes and black dyes; and as a result, we succeeded in obtaining inkjet color images having high quality and high fastness comparable to those of the current silver halide photos. In future, our studies are expected to be further applied to development of high-durability dyes for various applications.

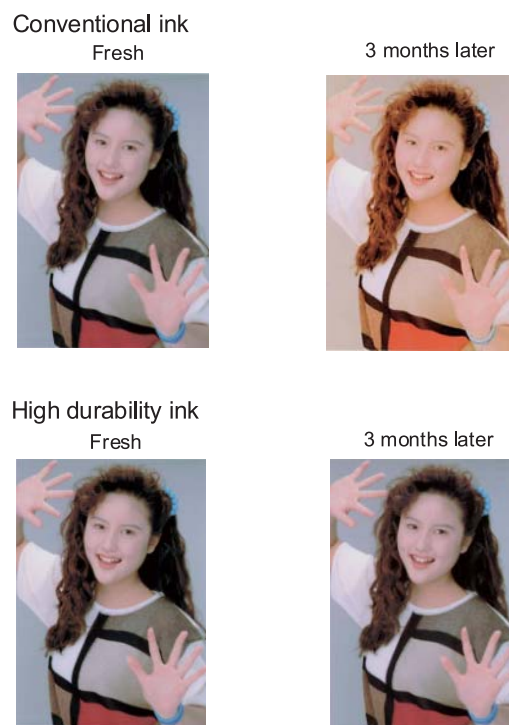


Fig. 9 Ozone-fastness comparison between conventional ink and high-durability ink comprising cyan dye C-1 and magenta dye M-1.

Acknowledgement

The present development was completed on the basis of many novel technical developments generated through collaboration with synthetic researchers, analytical researchers, and other members for ink development and evaluations in FUJIFILM Corporation. Regarding the stable production of high-purity dyes, we express our appreciation for the members in the Odawara Factory, Chemicals Production Section (now Chemicals Department) and the members in the related companies.

Fig. 3 and Fig. 9 in this report were reprinted from the Journal of the Association of Organic Synthetic Chemistry, Vol. 67, No. 1, as accepted by the Association of Organic Synthetic Chemistry of Japan.

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