Kirk-Othmer Encyclopedia of Chemical Technology.

FLUORESCENT PIGMENTS (DAYLIGHT)

There are many types of luminescent materials, some of which require a special source of excitation such as an electric discharge or ultraviolet radiation. Daylight-fluorescent pigments, in contrast, require no artificially generated energy. Daylight, or an equivalent white light, can excite these unique materials not only to reflect colored light selectively, but to give off an extra glow of fluorescent light, often with high efficiency and surprising brilliance. These pigments can also be excited with both short- and long-wave ultraviolet light. The use of a black light markedly increases the brilliance of the pigments, which makes them useful as tracers in many different applications.

Fluorescent pigments are comprised of dyed organic polymers. These polymers are clear and colorless and are formulated to be a solvent for the fluorescent dyestuff. There are many different chemical types of polymers and dyestuffs. In this article, the term dye applies to any organic substance that exhibits strong absorption of light in the visible or even ultraviolet region of the spectrum without regard to any affinity for textile fibers, paper, or other substrates (see Dyes, application and evaluation).

A fluorescent substance is one that absorbs radiant energy of certain wavelengths and, after a fleeting instant, gives off part of the absorbed energy as quanta of longer wavelengths. In contrast to ordinary colors in which the absorbed energy degrades entirely to heat, light emitted from a fluorescent color adds to the light returned by simple reflection to give the extra glow characteristic of a daylight fluorescent material. This fluorescence phenomenon can lead to reflectance values greater than 100% in a specific part of the spectrum.

1. History

1.1. Fluorescent Dyestuffs

Very few dyes are of use in making daylight-fluorescent products. Of the dyes discovered up to 1920, only the brilliant red and salmon dyes of the rhodamine and rosamine classes are used in fluorescent materials in the 1990s. The first of these, Rhodamine B, was discovered in 1877. Fluorescence excited by both uv and visible light components in daylight was formally recognized as a notable property of certain dyed fabrics by the 1920s (1).

The early yellow dyes, including Auramine O and Thioflavine T, were found to be extremely fugitive to light. However, in 1927 the first of the naphthalimide yellows, Brilliant Sulfoflavine FF [2391-30-2] (CI Acid Yellow 7), was discovered at I.G. Farben (2), followed by Azosol Brilliant Yellow 6GF [2478-20-8] (CI Solvent Yellow 44) (3). These two greenish yellow fluorescing dyes produced for the first time workable, bright, clean, fluorescent colors in the yellow range. They were by no means lightfast but at least were a great improvement over the earlier yellows. In addition, in mixtures with rhodamines, they formed bright orange and orange-red lacquers.

Table 1. Important Dyestuffs for Daylight-Fluorescent Pigments

Colour Index name	CAS Registry Number	Selected manufacturers
Basic Violet 11	[2390-63-8]	BASF, others
Basic Violet 10	[81-88-9]	BASF
Basic Red 1	[989-38-8]	L. B. Holliday, BASF, others
Acid Red 52	[3520-42-1]	Sandoz Chemical
Solvent Yellow 44	[2478-20-8]	L. B. Holliday
Basic Yellow 40	[12221-86-2]	Ciba-Geigy, L. B. Holliday
Solvent Yellow 135		Day-Glo Color Corp., L. B. Holliday
Solvent Yellow 160:1	[61902-43-0]	Day-Glo Color Corp. Bayer AG

In the 1930s, fluorescent-colored lacquers were used in theaters for special effects under black light (long-wave uv light), and the outstanding brilliance of the colors in simple daylight as well as their potential for outdoor advertising was recognized. This was followed by the preparation of dyed resinous pigments.

An important advance with regard to light stability was made with a group of yellow coumarin dyes with heterocyclic systems attached to the coumarin nucleus (4), eg, a greenish yellow cationic dye that is sold under the name Maxilon Brilliant Flavine 10 GFF [12221-86-2] (Blue Wool #4), designated CI Basic Yellow 40, available from several manufacturers.

Benzothioxanthene and benzoxanthene dyes, discovered by Farbwerke Hoechst AG (5–8) in the mid-1960s, have been employed to some extent in fluorescent pigments. Some members of this group have good color strength and very good lightfastness. Table 1 lists some of the important dyestuffs still used for daylight-fluorescent pigments.

1.2. Fluorescent Pigments

The first patents for daylight fluorescent products were issued in 1947 (9, 10), describing fluorescent dyed cellulose acetate fabrics with several barrier coats to improve long-term stability. These fabrics were brilliantly fluorescent and were widely used during World War II as signal panels.

Later, the manufacture of a thermoset pigment was patented (11). The polymer was dyed with fluorescent dyes and pulverized into a fine powder that could be used as a fluorescent pigment. The following procedure was employed: Solvent Yellow 44 was dissolved in a solution of butanol-modified urea–formaldehyde, the resin slowly heated to 90°C and gelled by the addition of acid, followed by post-curing at 140–145°C. The thermoset product was ball- or hammer-milled to the required fineness. This type of fluorescent thermoset resinous material had poor lightfastness, was difficult to grind, and was highly sensitive to environmental moisture.

Early fluorescent pigments were promoted and adopted for use in screen inks for poster boards and paints for safety applications. These thermoset pigments were not well-suited because of their poor lightfastness. Also, because of their relatively coarse particle size, their use in thinner film applications, such as gravure or flexo, was limited.

The performance of daylight-fluorescent pigments has steadily improved since their first large-scale manufacture. Modification with toluenesulfonamide yielded thermoplastic resins (12). These pigments were fused and condensed completely in the reaction kettle and, after cooling, were finely ground into pigments. This procedure greatly improved both water resistance and lightfastness.

These thermoplastic pigments found application in a much wider range of finished products. New, large-volume applications included coated paper for labels and point of purchase signage, gravure for soap box cartons and bright textiles for fashion, and safety applications.

Table 2. Commercial Fluorescent Products

	Manufacturer's code				
Pigment characteristics	Day-Glo	Lawter	Radiant	Sinloihi	Dane
single strength[a]	A	B-3500	R-105, R-103	FZ-2000	A
high strength[a]	AX	D-3000	R-106, R-104	FZ-4000	E
single strength[a] thermoset	T		P-1600	FZ-3000	T
high strength thermoset[a]	GT	TS	P-1700	FZ-3040	GT
high heat resistance, high lightfastness for plastics	ZQ, NX	TC	K-600		ZN
toners soluble in polar solvents	HM, HMS	HVT	GF	FM-10, FM-70	ST-EBT
paste concentrate bases for litho and letterpress	SFB	Optichrome 8600	Visiprint, VF	BO	OLC
high strength for vinyl	VC		K-500		
alkali water-soluble toners	WST		Aquabest		
fine particle size pigments	EP/EPX	SG-2500	JST	SW	

[a] Standard fineness.

Recent pigment technology has yielded a wide range of products which are much more specialized for individual end use applications. New polymers have been combined with improved dyestuffs to yield fluorescent pigments with better performance properties and economics, and more desirable environmental characteristics.

2. Availability

The primary manufacturers of daylight-fluorescent pigment at the present time are Dane and Co. (London); Day-Glo Color Corp. (Cleveland, Ohio); Nippon Keiko Kagaku Co. Ltd. (Tokyo); Nippon Shokubai (Osaka); Lawter Chemical Corp. (Skokie, Illinois); Radiant Color, Division of Magruder (Elizabeth, New Jersey); Sinloihi Co., Ltd. (Kamakura, Japan); and U.K. Seung (Busan, Korea). Smaller regional manufacturers are located in China, India, Russia, and Brazil.

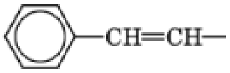
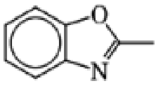
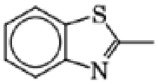
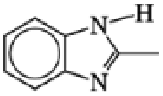
Table 2 lists fluorescent product lines marketed by various manufacturers, where similarities are known. New products are introduced and old products obsoleted on a regular basis.

3. Theory of Fluorescence

3.1. Structure

Virtually all important dyes contain aromatic rings in their structures. According to the theory, groups called chromophores have to be present on benzenoid rings in order for compounds to have appreciable light absorption or color. Certain basic groups, so-called auxochromes, are also necessary to bring out or intensify the color. The electronic theory of atoms and molecules, wave mechanics, and the theories of valence-bond resonance and molecular orbitals have increased the understanding of colored and fluorescent substances and their interaction with light. The benzene ring with its six π-electrons can act in conjunction with electron-donating groups (auxochromes) and electron-accepting (unsaturated) groups to produce strong absorption in the uv or visible regions which may give rise to fluorescence. Such a system of atoms, responsible for significant absorption of photons in the uv or visible regions, is referred to as a chromogen. A chromogen that absorbs in the uv as a rule can be modified chemically to absorb visible light, thus becoming colored. This is often

Table 3. Donor and Acceptor Groups in Fluorescent Dye Molecules

Electron–donor groups		Electron–acceptor groups	
strong		cyano	$—C\equiv N$
amino	H_2N—	carbonyl	
alkylamino	RHN—	vinylene	$—CH{=}CH—$
dialkylamino	R_1R_2N—	styryl	
oxido	—O—	acrylic ester	$—CH{=}CH—COOR$
weak		β-methacrylic ester	$—C(CH_3){=}CH—COOR$
hydroxy	HO—	benzoxazolyl	
alkoxy	RO—	benzothiazolyl	
		benzimidazolyl	

accomplished by adding benzene rings to the molecule or introducing a long unsaturated chain of atoms (see Chromogenic materials, photochromic).

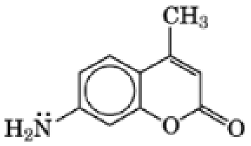
3.2. Chromogens

Organic dyes can be divided into four classes, depending on the type of chromogen or unsaturated system present: (*1*) $n \longrightarrow \pi^*$ chromogens, (*2*) donor–acceptor chromogens, (*3*) cyanine-type chromogens, and (*4*) acyclic and cyclic polyene chromogens (13). Almost all strongly fluorescent dyes fall into classes (*2*) and (*3*), whereas only a few have cyclic polyene chromogens of groups (*4*). The chromogens of class (*1*) are detrimental to fluorescence.

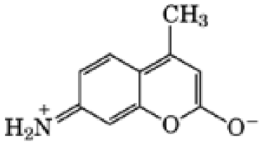
3.2.1. Donors and Acceptors

Table 3 lists common electron–donor groups, and electron–acceptor groups selected from a large number capable of evoking fluorescence.

In dyes in which a particular benzene ring carries a donor and an acceptor group, these groups are introduced in positions ortho or para to each other. In condensed ring systems such as naphthalene, conjugated-bond paths between donors and acceptors are necessary for interaction. These conditions are the rule rather than the exception also for nonfluorescent dyes. For example, the donor amino group in 7-amino-4-methylcoumarin [26093-31-2] **(1)** shares its lone pair of electrons with the benzene ring; the α, β-unsaturated ester group accepts electrons from the benzene ring. If the donor and the acceptor are in a para position to each other, as they are here, a partial electron displacement toward the carbonyl oxygen atom takes place. Absorption of a photon of uv light carries this displacement even further toward the high energy polarized form **(2)**. Fluorescence occurs if the molecule emits a photon of light in a transition from its first excited singlet state. The singlet state refers to a condition of paired spins for an even number of electrons in a molecule.



(1)



(2)

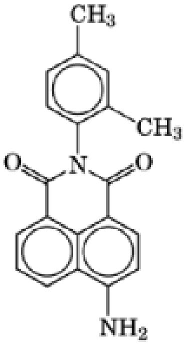
Donor–acceptor molecules are often sensitive to pH changes. For example, if acid is added to a solution of **(1)**, the lone pair of electrons on the nitrogen takes up a hydrogen ion forming a substituted ammonium salt. In the salt form, the nitrogen cannot conjugate with the benzene ring, and hence the fluorescence capability is strongly reduced. Addition of an alkali to the salt causes removal of the hydrogen ion and immediately restores the fluorescence under ultraviolet light.

Alkylation of the amino group to a mono- or dialkyl form strengthens the uv absorption and also increases the wavelength of the fluorescent light; two alkyl groups are more effective than one and ethyl groups are more powerful than methyl groups.

Hydroxy groups are very weak donors to the benzene ring. However, on treatment with alkali they form strongly donating ionized oxido groups (or phenolate ions when attached to the benzene ring). The strongly fluorescent alkaline solutions of 7-hydroxycoumarin [93-35-6] and fluorescein [2321-07-5] are examples. Neutralizing with acid quickly destroys the fluorescence almost completely. Even dilution with water causes gradual weakening of the fluorescence by hydrolysis.

If the hydrogen atom of a hydroxy group becomes hydrogen bonded to an ortho-substituted group, appreciable or even strong fluorescence can be evoked. For example, the crystalline yellow fluorescent pigment, the azine of 2-hydroxynaphthaldehyde-1 (14), is sold as Lumogen Light Yellow L [2387-03-3] by BASF. It performs well in applications under ultraviolet light, but is not stable enough for daylight exposure.

Alkylation of donor amino groups strengthens them as donors but usually reduces lightfastness. CI Solvent Yellow 44 [2478-20-8] **(3)** has already been mentioned as a dye for daylight-fluorescent pigments, but its lightfastness is only fair (Blue Wool Scale 2–3). It has been a component of green, yellow, orange, and red pigments for many years. The monoalkylamino compound, CI Solvent Yellow 43 [12226-96-9] **(4)**, is also available. It is appreciably redder and stronger than unsubstituted **(3)** but poorer in light stability (Blue Wool Scale 2.0).



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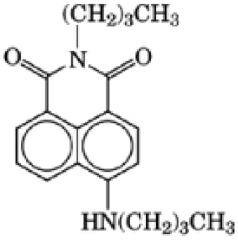
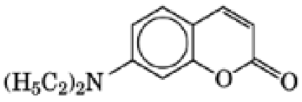


(4)

In these dyestuffs, the two carbonyl groups are acceptors; the aryl group is that of naphthalene. The one obvious para conjugation between the amino group and the carbonyl group is hardly sufficient to explain the moderately strong absorption in the blue and violet region that occurs in these dyes. There is probably some conjugation between the groups on the 4 and 8 positions of the naphthalene structure.

Greater depth of color in a chromogen can be obtained by providing a more complex acceptor group or linear addition of acceptor groups. Thus the 7-diethylaminocoumarin [20571-42-0] **(5)** is colorless with a blue fluorescence, whereas Coumarin 7 [27425-55-4] **(6)** is yellow with a green fluorescence. The conjugation in structure ***(6)*** includes the benzene ring fused to imidazole. By methylating both nitrogen atoms of the imidazole ring, a yellow of better light stability for nonalkaline substrates is obtained, Basic Yellow 40 [12227-86-2] **(7)**.



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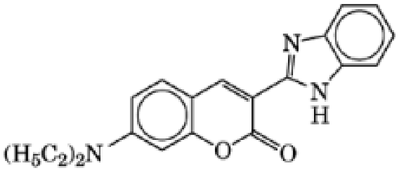

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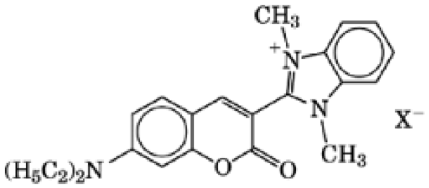


(7)

Donor–acceptor chromogens in solution are often strongly affected by the nature of the solvent or the resinous substrate in which they are dissolved. The more polar the solvent or resin, the longer the wavelength of the fluorescent light emitted. Progressing from less polar to more polar solvents, the bathochromic, or reddening, effect of the solvents on the dye increases in the order of aliphatics $<$ aromatics $<$ esters $<$ alcohols $<$ amides.

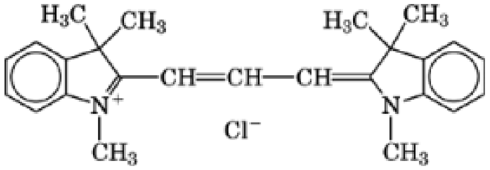
3.2.2. Cyanine Types

Cyanine-type chromogens are odd-alternate systems that have at least two equivalent or nearly equivalent resonance forms (13). Open-chain cationic chromogens of this class are represented by **(8)** and can be viewed as true cyanines (see Cyanine dyes). If the two terminal atoms were oxygen instead of nitrogen, the system would be a cyanine-type chromogen. In each of these forms, one oxygen atom would carry a negative charge.

$$R_2\ddot{N}{-}(CH{=}CH)_n{-}CH{=}\overset{+}{N}R_2 \quad X^- \longleftrightarrow R_2\overset{+}{N}{=}CH{-}(CH{=}CH)_n{-}\ddot{N}R_2 \quad X^-$$

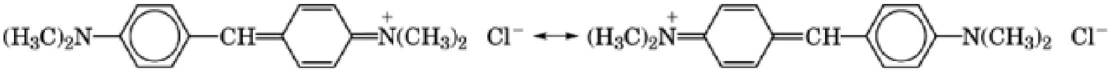
(8)

In most true cyanines the nitrogen atoms are part of heterocyclic rings. Astra-phloxine FF [6320-14-5] **(9)**, CI Basic Red 12, is a true cyanine in the modern sense and is strongly fluorescent in the red region. Its light stability is not as good as that of Rhodamine B. Chromogens of the odd-alternate types such as **(8)** and **(9)** have nonbonding molecular orbitals extending along the conjugated chain. The cyanines thus have completely delocalized electrons, a situation quite different from that in the donor–acceptor chromogens.



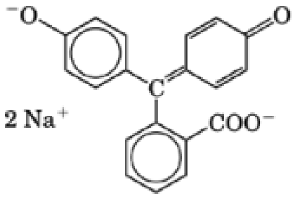
(9)

There are good reasons to consider extending the class of cyanine-type chromogens to the older and well-known group of basic dyes (15). In a diphenylmethane dye such as Michler's Hydrol Blue **(10)**, one ring contributes two double bonds in order to give an odd-alternate system. Aromatic-ring systems can be made part of the conjugated chain of a cyanine without altering the characteristic properties of the chromogen (13, 16).



(10)

None of the simple di- and triarylmethane dyes, with the exception of the auramines, have strong fluorescence (see Tiphenylmethane dyes). For example, the well-known indicator phenolphthalein [518-57-4] has a nonfluorescent strongly red alkaline form **(11)**. However, if an oxygen bridge is introduced between the upper benzene rings, the intensely green fluorescing alkaline form of fluorescein disodium salt [578-47-8] **(12)** results.



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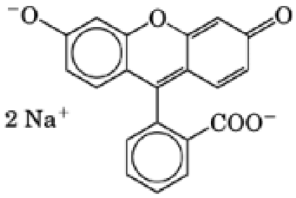
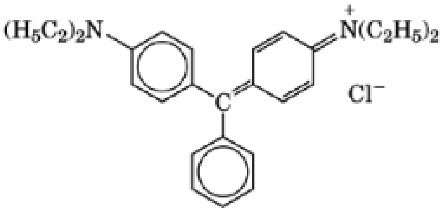


(12)

The alkyl and dialkylamino compounds are much more important. If the structure of Brilliant Green [633-03-4] **(13)** (CI Basic Green 1) is altered by inserting an oxygen bridge and a carboxyl group on the lower ring, the brilliant red-fluorescing Rhodamine B [81-88-9] **(14)** is formed.



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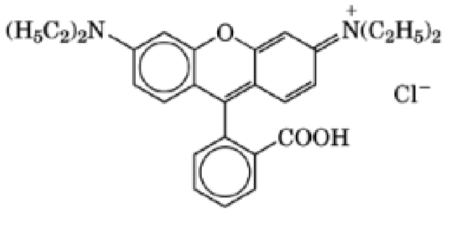
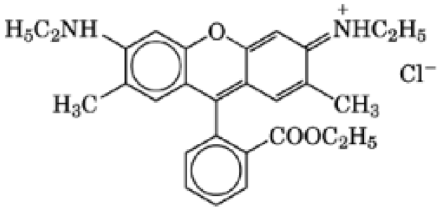


(14)

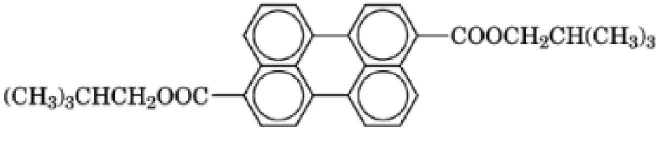
In Rhodamine 6G, also sold as Rhodamine F5G [989-38-8] **(15)**, the carboxy ester group prevents free rotation of the lower phenyl group. Its position is roughly perpendicular to the plane of the other three rings. Retention of color strength is good because there is less electronic interaction between the lower ring and the rest of the molecule.



(15)

3.2.3. Cyclic Polyenes

Polycyclic aromatic hydrocarbons, including cyclic polyene chromogens, are not represented among current daylight-fluorescent dyes. Compounds with more than two or three rings are often carcinogenic. However, derivatives with electron-withdrawing groups offer some definite possibilities, as, for example, the commercial dye Thermoplast Brilliant Yellow 10G [2744-50-5] **(16)** (CI Solvent Green 5) which gives brilliant green fluorescent solutions.



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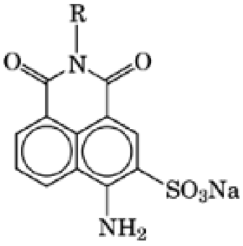
3.3. Groups Detrimental to Fluorescence

Strong fluorescence is prevented by nitro and azo groups, the latter being very common in dyes (see Azo dyes). Because of its high electronegativity, the fluorine atom has a strong electron-withdrawing effect. If the fluorine is present on a benzene ring carrying a donor group, the inductive action is sufficient to practically eliminate the possibility of fluorescence. A trifluoromethyl group substituted for methyl attached to the acceptor group, however, increases the light stability of several laser dyes (17). Bromine and iodine atoms in almost any position weaken fluorescence by accepting electronic energy of excitation and converting it into heat.

Sulfonation increases the water solubility of dyes. A sulfonic group is electron withdrawing but has a weakening effect on the fluorescence only if it is ortho to the donor group. For example, in Brilliant Sulfoflavine

FF [2391-30-2] **(17)**, where R = p-tolyl,—$C_6H_4CH_3$, it has a weakening effect, although the cleanness of the fluorescent color is somewhat improved compared to that of the unsulfonated compound.

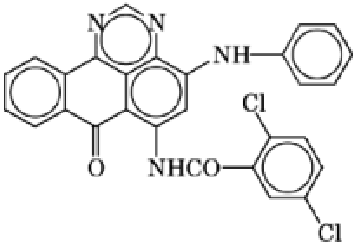


(17)

Dyes containing a dominant benzoquinone group are generally nonfluorescent. The anthraquinones, for example, are almost completely without fluorescence (see Dyes, anthraquinone).

3.4. Rigidity and Fluorescence

The more rigid the molecule, the less likely that low energy vibrations are initiated by transfer of energy from the first excited singlet state before fluorescence can take place. A small class of dyes, the pyrimidanthrones, in which one of the quinone oxygen atoms is replaced by nitrogen and the latter made part of a rigid ring, for example, are strongly fluorescent. One of them, Lumogen L Red Orange [6871-91-6] **(18)** is a crystalline substance with a deep red-orange fluorescence.



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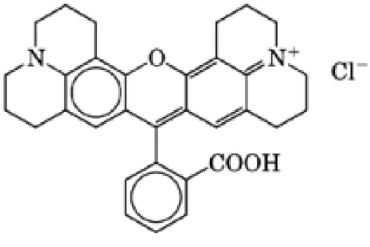

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The effect of forming a more rigid structure in fluorescent dyes of the rhodamine series has been clearly demonstrated (18) with the remarkable dye designated Rhodamine 101 [41175-43-3] **(19)**. This dye has its

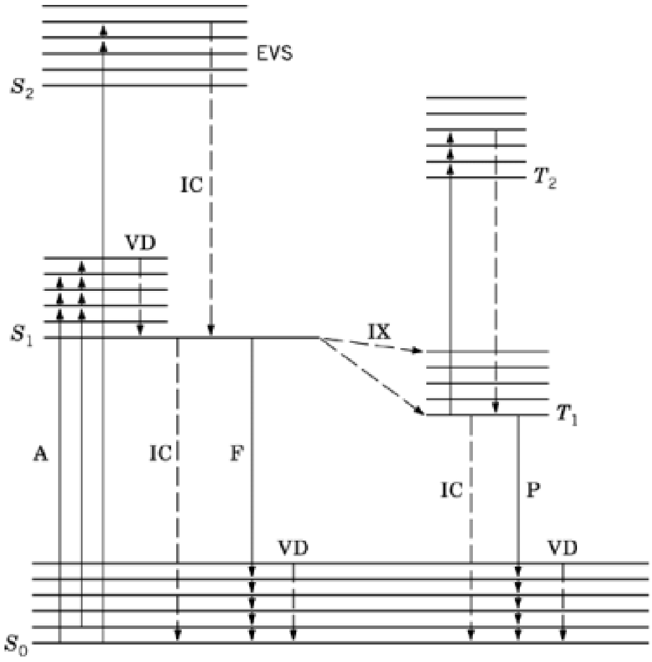

Fig. 1. Schematic energy-level diagram for a dye molecule. Electronic states: S_0=ground singlet state; S_1=first excited singlet state; S_2=second excited singlet state; T_1=first excited triplet state; T_2=second excited triplet state; EVS=excited vibrational states. Transitions: A=absorption excited states; VD=vibrational deactivation; IC=internal conversion; F=fluorescence; IX=intersystem crossing; and P=phosphorescence.

terminal nitrogen atoms each held in two rings and has a fluorescence quantum yield of virtually 100% independent of the temperature.

3.5. Energy Levels and Light Absorption

A dye molecule of about 50 atoms would have ca 150 normal vibrations of the molecular skeleton (15). Figure 1 shows the typical transition between various energy states that the π-electrons of a dye molecule can undergo. The singlet ground state of the π-electrons in the molecule is designated S_0 and represents the lowest electronic energy level possible for the molecule. The molecule can be excited to higher electronic states such as S_1 or S_2 with an associated set of vibrational energy levels represented by a series of lines above the particular electronic level.

In the process of excitation, the dye molecule absorbs a quantum of uv or visible radiation. The quantum has an energy $E = h\upsilon$, where h is Planck's constant and υ is the frequency of the radiation. The higher the frequency of the quantum, the shorter the wavelength λ, with $\upsilon \cdot \lambda = c$, where c is the velocity of light in a vacuum.

If, as is usually the case, it is a π-electron that is raised in energy by the quantum or photon from the S_0 state to the S_1 state, the electron is said to undergo a $\pi \longrightarrow \pi^*$ transition. Because the quantum is totally absorbed, the π-electron is raised in energy by exactly the same amount as the energy of the quantum.

The new orbital of the π-electron in the π^*-state is larger than it was in the unexcited state. The two adjacent atoms with which the electron was associated in the ground state may be partially held by the electron in its expanded π^*-orbital. The atoms, in adjusting to the new binding condition, must move farther apart. They absorb the energy necessary to do this from the electron in its π^*-orbital. An additional vibrational amplitude is attained by the two atoms as a system. Some added energy is transmitted to other atoms of the conjugated molecule. These atomic vibrational adjustments take place very quickly, in 10^{-13} to 10^{-11} s.

In addition to interatomic vibrations, groups of atoms in the molecule can have a number of rotational energy levels which add to the number of possible levels of total energy of the chromogenic system. Association of various atoms of the molecule with polar solvents, for example, can also alter the degree of conjugation of the interrelated system. These added influences, which can also change from instant to instant, result in an enormous number of different energy levels in the billions of molecules of a particular irradiated sample. The excited states are also affected by the same influences. As a result, the molecule can be in any one of a very large number of total energy levels.

Because, in principle, transitions can occur on light absorption to any of the many possible energy levels of the excited state from any one of the many possible energy levels of the ground state, the absorption spectrum of a chromogen at room temperature or above is virtually continuous.

3.5.1. Fluorescence from the Excited S_1 State

In Figure 1, after absorption (A) and vibrational deactivation (VD) occur, the lowest or nearly lowest level of the singlet excited state S_1 is reached. If the molecule is fluorescent with a high quantum efficiency, fluorescent emission of a quantum of light generally occurs, indicated by fluorescence (F). Readjustment of some bond lengths of the chromogenic skeleton very likely would have to occur before reaching the lowest possible vibrational state consistent with the temperature of the surrounding medium. Thus the photon of light given off would not in general be equal to the quantity $S_1 - S_0$ but would be less, because the emission of the photon would complete the process.

If the incident photon has sufficient energy to excite the electron to the second state S_2, another process comes into play. The S_2 state has a very short lifetime of less than 10^{-11} s. Part of the energy of the S_2 state is converted rapidly to interatomic vibrations which quickly lose energy to other parts of the molecule or to surrounding molecules. This process is called internal conversion (IC) and is nonradiative. However, the electron energy loss is not total. The system generally attains the S_1 state from which fluorescence or other transitions can occur. The S_3 and higher singlet states are also subject to internal conversion, all such states having the possibility of losing energy to give the S_1 state from which a fluorescence quantum can be given off. The S_1 state can last as long as 10^{-8} s, a period long enough for fluorescence to occur.

Because fluorescence takes place only after the system has reached the S_1 state, regardless of the energy of the absorbed radiation, the fluorescence emission spectrum is independent of the wavelength of the absorbed light. The two requirements for the incident radiation is that it be high enough in energy to excite the dye molecule to the S_1 state but not so high that it causes decomposition of the dye.

Because the drop in energy of the molecule that occurs on emitting a fluorescent photon is generally less than the energy of the absorbed photon, the wavelength of the fluorescent light is almost invariably longer than the wavelength of the exciting light. This is Stoke's law, and applies in almost all cases of fluorescence.

Fluorescent photons can vary widely in energy, even if emission occurs from the same type of dye molecule. As a result, the emission spectrum of a typical dye is quite broad, frequently extending for 150 nm.

3.5.2. Competing Processes from the S_1 State

It can be seen from Figure 1 that transitions other than fluorescence can take place from the S_1 state. The molecule can lose electronic energy by internal conversion, passing through a higher vibrational level of the S_0 state, before undergoing vibrational deactivation by surrounding molecules. The electronic excitation energy can also pass by intersystem crossing (IX) to one of the levels of the first excited triplet state, characterized by two unpaired electrons with parallel spins.

The triplet state has the relatively long lifetime of 10^{-4} s or more. When emission occurs from the triplet state, it is called phosphorescence (P). Inorganic materials can exhibit phosphorescence after a delay as long as several hours but with dyestuffs in resins any delay is quite short. That the excited triplet state persists as long as it does in a phosphorescent organic compound is due to the fact that one of the electrons must reverse its spin before or during its transition to the ground state. The process $T_1 \longrightarrow S_0$ is not an allowed transition according to quantum mechanics. As a result, the probability of occurrence is small and the lifetime of the triplet state is relatively long. Because of the relatively long lifetime of the first excited triplet state, the possibility of chemical reaction or photochemical breakdown of the molecule takes on added weight for those dyes that are prone to triplet-state formation. Such dyes could have poor lightfastness.

In addition to the processes that can compete with fluorescence within the molecule itself, external actions can rob the molecule of excitation energy. Such an action or process is referred to as quenching. Quenching of fluorescence can occur because the dye system is too warm, which is a very common phenomenon. Solvents, particularly those that contain heavy atoms such as bromine or groups that are detrimental to fluorescence in a dye molecule, eg, the nitro group, are often capable of quenching fluorescence as are nonfluorescent dye molecules.

A high concentration of the fluorescent dye itself in a solvent or matrix causes concentration quenching. Rhodamine dyes exhibit appreciable concentration quenching above 1.0%. Yellow dyes, on the other hand, can be carried to 5 or even 10% in a suitable matrix before an excessive dulling effect, characteristic of this type of quenching, occurs. Dimerization of some dyes, particularly those with ionic charges on the molecules, can produce nonfluorescent species.

A nearby molecule with a conjugated system may rob the dye molecule of its electronic energy. On the other hand, a fluorescent dye can pick up electronic energy from such a substance, called a sensitizer, with increased fluorescence.

Radiation, both in the uv and in the visible region, can have a highly destructive effect by decomposing the dye molecule. Other substances, particularly water, can reinforce the photochemical effect of light. Once the dyed material fades, its original condition usually cannot be restored. Sometimes a darker material forms that bleaches on further exposure to the incident light. In any case, reasonable stability to light is one of the most important requisites of a useful fluorescent pigment, but the most difficult to achieve. An interesting discussion of the products of photolysis of 4-methyl-7-diethylaminocoumarin [91-44-1] is given in Reference 19.

The effect of the molecular matrix in which the dye is dissolved is of great significance. Matrices vary greatly in their effect in making a dye light resistant. Rigid polymeric media can have a beneficial effect on a fluorescent dye by reducing intermolecular motion and energy transfer.

Whereas the earliest fluorescent-dye pigments would last only 20 days outdoors in a screen-ink film, fade resistance has been improved to such an extent that some modern daylight-fluorescent coated panels still have useful color after nine months or more in Florida sunlight in a 45° exposure rack facing south. The fluorescent layer is usually coated with an acrylic film containing a uv absorber. Indoor-accelerated exposure equipment is, of course, invaluable in the development of such systems. Better dyes and resins very likely will make possible far more stable coatings in the future.

When measuring the lightfastness of fluorescent materials it is important to keep in mind several criteria. Lightfastness is dependent upon the type of pigment used, the concentration of the pigment in the test specimen, the thickness of the specimen, the composition of the specimen in which the pigment is dispersed or dissolved, any additives to the specimen, the substrate the specimen is coated on if any, and any overcoats used to protect the specimen. In general, the greater the concentration of the pigment the greater the lightfastness, the thicker the specimen the greater the lightfastness, and in some cases additives such as light stabilizers and antioxidants (qv) can have beneficial effects. Such additives are most beneficial when used in an overcoat to protect the pigment. Additives which have a detrimental effect are metals such as iron and zinc, and oxidizing chemicals.

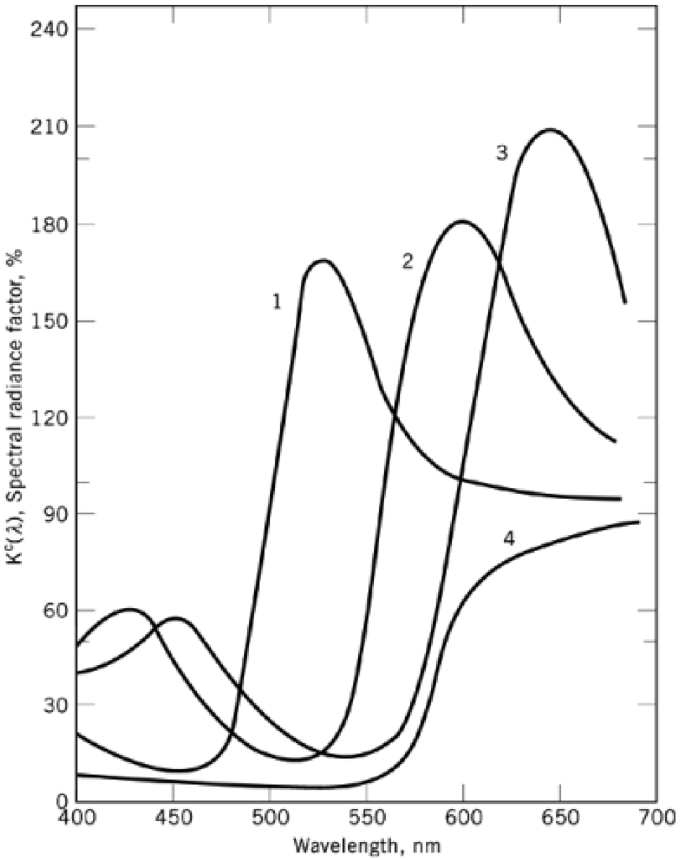

Fig. 2. Curves 1, 2, and 3 show the spectral radiance factor for equivalent coatings of separate toluenesulfonamide–melamine–formaldehyde Day-Glo pigments containing 0.5% of a dye, either Alberta Yellow, Rhodamine F5G, or Rhodamine B Extra. Curve 4 is for a bright nonfluorescent red-orange printing ink. The illuminant was Source C. A magnesium oxide-coated block was used as a comparison white.

4. Color Formation

4.1. Spectral-Energy-Ratio Curves

Figure 2 shows the spectral-energy-ratio curves of three daylight-fluorescent dyes in pigment drawdowns, ie, paint samples drawn down with a bar on special panels, and a curve for a nonfluorescent ink. The lower left part of each of the first three curves is essentially the same as the transmittance or reflectance spectrum of the dye. If these were nonfluorescent dyes, the absorbed energy of the incident daylight would all be lost as heat and at no point could the curve rise above 100%. With a strongly fluorescent substance, however, most of the absorbed energy is stored in the S_1 excited state and is largely given off as fluorescent light of longer wavelengths covering a considerable range.

For example, the greenish yellow coumarin dye, Alberta Yellow (curve 1) has a nonfluorescent reflection of 75 to 80%, but emitted fluorescent light adds to reflected light to give a peak radiance factor of 177%. This means that there is 77% more green light of 525 nm returned from the sample than there is green light of that wavelength in the white light falling on the sample. The result is that the human eye and brain which adds the effects of light of all wavelengths in the visible region sees a very bright greenish yellow. Because the eye is especially sensitive in the yellow-green region, the luminance factor, which takes into account the sensitivity of the eye to all wavelengths, is 123%, or 23% brighter than the purest white. The same yellow dye is the starting point for a bright fluorescent green pigment. Simple addition of a nonfluorescent phthalocyanine green toner in aqueous dispersion in the pigment-forming process cuts out important orange and red components of the yellow dye resulting in a bright daylight fluorescent green.

4.2. Effect of Two or More Dyes

A most remarkable effect in daylight fluorescence, the transfer of energy from one fluorescent dye to another, can be used to produce colors more brilliant for their particular spectral regions than one dye alone could produce. If Rhodamine F5G (Fig. 2, curve 2) is added to a pigment system based on Alberta Yellow and the finished pigment drawdown exposed to white light, the energy stored momentarily by the yellow dye passes to the F5G dye either by emission and reabsorption or by direct energetic excitation. If the latter occurs, the yellow dye would be acting as a sensitizer for the F5G. A much greater peak height of the radiance factor curve results. At the same time, the yellow dye absorbs so powerfully in the violet region that the blue-violet component of the salmon curve 2 is eliminated. A very bright orange is formed. Addition of a small amount of Rhodamine F3B can displace the peak further toward the red, giving a color with the highest peak of all of the colors, for example, Day-Glo Blaze Orange. This phenomenon of energy transfer from one molecule to another gives the fluorescent pigments their brilliance but also leads to problems in using conventional color matching equipment to give accurate values to fluorescent pigments.

Rhodamine F3B (Fig. 2, curve 3) can also participate strongly in the energy-transfer effect, receiving energy from both the greenish yellow and the salmon dyes. The blue and violet components of the Rhodamine F3B are also reduced, resulting in strong bright red-oranges and reds. Pinks and deep bluish reds are produced essentially with Rhodamine F3B. For comparison, curve 4 (Fig. 2) shows the reflectance of a bright nonfluorescent printing ink. It is possible for multiple-dye-pigmented coatings applied over a white surface to show peak radiance factors of nearly 300%.

5. Methods of Manufacturing

5.1. Bulk Pigment Polymerization

Most fluorescent pigments are of the toluenesulfonamide–melamine–formaldehyde resin matrix type. The following general technique is used (12). A mixture of *o*- and *p*-toluenesulfonamide, paraformaldehyde, and a B-stage unmodified melamine–formaldehyde resin is heated at ca 170°C for about 15 minutes (see Amino resins). Rhodamine F3B (CI Basic Violet 11), Rhodamine 6GDN Extra (Basic Red 1), and Brilliant Yellow 6G Base (Solvent Yellow 44) are added and heating continued. Upon cooling, the completely condensed resin solidifies at about 115°C. The finished colored resin is clear, brittle, and friable. It has a fiery red-orange color and is highly daylight fluorescent. The resin mass can be pulverized by impact milling to a fine powder, which is the final fluorescent pigment and is used in a wide variety of applications.

Post-curing and chemical modification improves chemical and solvent resistance (20). Paraformaldehyde and acetylene diurea are added to a hot borax solution. Toluenesulfonamide (*p* and *o*), a few drops of phosphorous acid, Brilliant Yellow 6G [2429-76-7], Rhodamine F3B, and Rhodamine 6GDN [989-38-8] are added. After heating, the mass is cured in an oven at 150°C. The resulting cured resin is thermoset but can be ground to fine particle sizes.

A polyamide-type resin matrix is claimed (21) to have superior heat resistance and be especially suitable for use in coloring plastics. The matrix is made of isophoronediamine and isophthalic acid; Rhodamine F3B is added above 200°C. Upon cooling, the mass solidifies to a friable resinous solid. This product, after grinding, is highly suitable for coloring plastics processed by injection molding. Products of this type are reported to be resistant to temperatures as high as 315°C for 10 minutes.

A polyester-type fluorescent resin matrix (22) is made by heating trimellitic anhydride, propylene glycol, and phthalic anhydride with catalytic amounts of sulfuric acid. Addition of Rhodamine BDC gives a bright bluish red fluorescent pigment soluble in DMF and methanol. It has a softening point of 118°C. Exceptional heat resistance and color brilliance are claimed for products of this type, which are useful for coloring plastics.

Another fluorescent pigment class (23) is based on a urethane-type resin; the primary raw materials are isocyanates, amines, and hydroxy compounds.

Several new types of pigments have been introduced commercially which are based on polymers that do not contain formaldehyde. These pigments have some different characteristics but have the advantage of not giving off formaldehyde. Most of the primary manufacturers provide these types of pigments and more are being developed.

5.2. Emulsion–Suspension Polymerized Pigment Ink

Polymerization of a polar prepolymer as the internal phase in an oil-based external phase (24) gives a fluorescent ink base in which spherical fluorescent particles are dispersed. This base is suitable for litho and letterpress inks (qv). An emulsion is formed from paraformaldehyde, *o*- and *p*-toluenesulfonamide, Solvent Yellow 44, and melamine with heating in an oil vehicle which forms the continuous external phase of the finished product. Rhodamine F3B and Rhodamine 6GDN are added under high speed agitation and heating. The oil vehicle is formed by blending 60 parts of a 50% styrenated-type alkyd solution at 50% solids in a high boiling ink oil (Magie 535) with 40 parts of bodied linseed oil.

5.3. Soluble Fluorescent Polymers

Several pigment manufacturers have developed fluorescent polymers intended to be used as a solution for application to various substrates. These toners come in both solvent soluble and alkaline water-soluble forms.

For example, Day-Glo HM Series toners come in a range of colors suitable for flexographic and gravure inks of the solvent-base type. The Radiant GF Series and Lawter HVT Series are also suitable for this type of application (see Table 2). Generally, these toners are of the formaldehyde–sulfonamide type and require oxygenated solvents, primarily alcohol–ester blends, for proper solution. For applications such as flexographic printing on film, these materials are modified with other resins such as nitrocellulose or polyamides in the finished ink.

In addition to the solvent soluble toners, alkali water-soluble toners have been produced. These types include WST produced by Day-Glo and Aquabest produced by Radiant Color. These toners are dissolved in water which contains a portion of ammonia and, if necessary, some isopropyl alcohol. These toners can be used as binders or additional binders and other additives can be added to give the ink the desired properties. These toners are condensation-type polymers other than the formaldehyde types.

Nippon Shokubai and U.K. Seung are producing a fluorescent polymer claimed to be made from a co-condensation of benzoguanamine and formaldehyde. Fine highly thermoset particles are manufactured in solution and later dried. It is useful in a wide range of applications, specifically plastics, and markets where bleed is a problem.

6. Economic Aspects

The market price of fluorescent pigments varies from ca \$9/kg for certain grades of material that might find application in the textile and paper coating industries, to over \$18/kg for special, high technology products with applications ranging from flexo and felt tip markers to plastics. Growth in the primary market segments such as packaging, safety, signage, toys, etc, approximate GNP growth in most of the world's regions, and new markets that are opening have seen substantially better growth.

The total world marketplace can vary widely from year to year, however, due to the cyclic nature of the textile and collateral applications which can be sizable but short-lived. Perhaps this is the reason that there are no published estimates for the world market for fluorescent color. Also, competition has forced most producers to develop higher strength fluorescent materials that offer greater color yield and a better money value. This reduces unit volume and, in many cases, dollar sales.

7. Application Properties and Uses

Fluorescent colors are remarkable for their extremely high visibility and their ability to attract attention, and applications utilizing these properties have gained the greatest acceptance. Advertising offers one of the main uses of fluorescent colors. Fluorescent billboards along highways, fluorescent packages at supermarkets, and fluorescent advertisements in magazines have all proven to be extremely effective ways of promoting consumer goods. The presence of the fluorescent color attracts the attention of the viewer earlier, holds their attention longer, and brings the consumer back for a second look more frequently than conventional color.

Another large field for fluorescent color is for safety uses. Fluorescent color has been particularly effective on vehicles, such as fire trucks, ambulances, and rescue equipment. Fluorescent color is far more visible than the equivalent hue of conventional color under all lighting conditions and is particularly valuable at dawn, dusk, and in overcast conditions. Fluorescent colors are used to mark off the boundaries of danger areas at construction sites and around heavy equipment, highlight safety equipment in industrial operations, as well as for highway traffic cones, flagging, and on worker safety vests. A large safety application for fluorescent colors is for hunters' and woodsmen's clothing during hunting season; in most states this is mandatory.

Fluorescent color also is used in the optical-sensing field and in the coding and tracing of documents and other items. This is not strictly a daylight-fluorescent use since there are many ultraviolet-responsive products that have virtually no daylight fluorescence. Daylight-fluorescent color has, however, become important in this field. Fluorescent inks are extremely useful in the high speed handling of documents, such as automatic sorting where a fluorescent mark on each document allows proper orientation and provides much improved efficiency compared with manual sorting.

The brilliance of daylight-fluorescent color finds use in most of the color consuming markets because of advances in use technologies. Markets served are injection molded toys, blow molded bottles, high speed sheet-fed and web-offset printing, gravure and flexo printing (water and solvent inks), industrial paint to tempra colors, felt tip pens, paper coating, textile printing and dyeing, plus a variety of specialty applications.

Table 4 shows daylight fluorescent pigments with approximately equivalent colors manufactured by U.S. manufacturers. In addition to the colorants listed, other colors are available such as purples and shades which are stronger and between the shades listed.

8. Commercial Properties of Fluorescent Pigments and Colorants

The largest percentage of commercial fluorescent pigments are made by bulk polymerization and are mechanically ground. The sulfonamide melamine–formaldehyde pigments generally have a density of 1.3 – 1.4 g/mL

Table 4. Commercial Pigment Colors, Standard Strength Pigments[a]

Day-Glo A-Series[b,c]	Lawter B-3500 Series[d]	Radiant R-105 Series[e]
A-17-N, Saturn Yellow	B-3539, lemon yellow	R-105-810, chartreuse
A-18-N, Signal Green	B-3545, green	R-105-811, green
A-16-N, Arc Yellow	B-3515, gold-yellow	R-105-812, orange-yellow
A-15-N, Blaze Orange	B-3514, yellow-orange	R-105-81, orange
A-14-N, Fire Orange	B-3513, red-orange	R-105-814, orange-red
A-13-N, Rocket Red	B-3534, red	R-105-815, red
A-12, Neon Red	B-3530, cerise red	R-105-816, cerise
A-11, Aurora Pink	B-3522, pink	R-105-817, pink
A-21, Corona Magenta	B-3554, magenta	R-103-G-188, magenta
A-19, Horizon Blue	B-3556, vivid blue	R-103-G-119, blue

[a] Similar colors are listed horizontally but are not exact color matches.
[b] These names are trademarks of Day-Glo Color Corp.
[c] Thermoplastic pigments for use in paint, screen ink, plastisol, gravure ink, paper coatings, and many other applications.
[d] Multipurpose pigments for paint, gravure ink, screen ink, paper coatings, plastisol, candles, plastics, and many other applications.
[e] Multipurpose pigments for paint, screen ink, paper coatings, plastisol, gravure ink, plastics, and many other applications.

and average particle sizes from 2.5 to 6 μm. Melting points of the thermoplastic types range from 110–140°C; the thermosets do not melt but soften in the range of 150–170°C. These pigments decompose at about 200°C.

The other mechanically ground pigments are of the ester, amide, and other condensation-type chemistries. The average particle sizes are similar to the formaldehyde types except for toners and some plastic pigments which are coarsely ground. Melting points range from 70 to 170°C depending on the chemistry; however, the density tends to be less than the formaldehyde, in the 1.15 to 1.25 g/mL range. Decomposition of these resins tends to occur between 250 and 300°C but color degradation starts at about 200°C. Special pigments for high temperature applications such as Radiant K and Day-Glo ZQ have been developed which have better color retention properties at elevated temperature. Various other pigments are available with many different properties, eg, particle sizes from the submicrometer range to coarse sand-like materials.

8.1. Plastics

Most manufacturers of fluorescent pigments offer special products for coloring thermoplastic molding resins. Low and high density polyethylene, high impact and general-purpose polystyrene, ABS, and various acrylic polymers are best suited for these pigments. The pigment, 1–2% of the total weight of the plastic, is added either as a dry-blended material or first formulated into a color-concentration pellet which is blended into the uncolored resin before molding into a finished article.

Products suitable for this type of use are Day-Glo ZQ-Series, vinyl colorant, and NX-Series pigments; Dane's ZN Series, Radiant's K-600 and K-7000 pigments; and Lawter's TC Series (see Table 2). These products are dramatic improvements over the toluenesulfonamide-modified melamine–formaldehyde-type resins, and are heat resistant up to 300°C when used in injection molding equipment; however, there is significant color shift with increasing temperature. They also exhibit improved light resistance and do not have the troublesome formaldehyde odor long associated with the use of fluorescent pigments in plastics. The NX-Series and ZQ-Series have dramatically reduced plateout over other fluorescent pigments, which makes them more like conventional pigments in certain plastic applications.

8.2. Paint

Fluorescent pigments in various types of paint offer an effective way to impart fluorescence. Because of the inferior lightfastness of fluorescent products in thin layers, the paint is generally applied in a 75–150-μm thick layer to optimize the resistance to exterior fading. For maximum color effect and durability, fluorescent paints should be applied over a high grade white substrate and overcoated with a clear uv-absorbing coating that virtually doubles the life of the color effect. The most commonly used paint systems are alkyd enamels or acrylic lacquers. For these paint systems, Day-Glo A or D, and AX Series, Radiant R-103-G, R-105, and R-203-G Series, and Lawter B-3500 Series are recommended. A formulation for an acrylic lacquer follows; it is thinned to spraying viscosity with xylene. The acrylic vehicle is 35% Acryloid B-66 (Rohm & Haas) and 65% SC-100.

High speed mix component	Wt %
acrylic vehicle	54.0
Cab-O-Sil M-5 (Cabot Corp.)	0.5
fluorescent pigment	38.0
SC-100	7.5
Total	*100.0*

8.2.1. Aerosol Paint

For aerosol paints, fluorescent pigments are available, including Day-Glo A and AX Series, Radiant R-105 and R-106 Series, and Lawter G-3000 Series. With new regulations from the U.S. Environmental Protection Agency (EPA) tightening the allowed VOCs, more recent formulas contain oxygenated solvents and can therefore require the use of a thermoset pigment such as the Day-Glo T or GT, Radiant P-1600 or P-1700, or Lawter TS Series. A typical starting formulation for a fluorescent aerosol paint concentration is given below. The finished canned material should consist of 55% thinned paint and 45% propellant.

High speed mix component	Wt %
Acryloid F-10, 40% in mineral thinner (Rohm & Haas)	45.5
fluorescent pigment	35.0
lactol spirits	17.7
toluene	1.8
Total	*100.0*

8.2.2. Water-Based Paint

Fluorescent pigments also have some use in water-based paint systems, with many being sensitive to aqueous media, especially at pH above 7.5. For extended shelf stability, Radiant P-1600 or P-1700 Series, Day-Glo T and GT pigments, and Sinloihi FZ-3000 Series are recommended.

8.3. Gravure Ink

Fluorescent pigments are used in liquid gravure inks. A fine particle sized pigment is incorporated into a vehicle system composed of a soluble nonoxidizing binder in volatile solvent. Pigments suitable for this type of application, depending on the nature of the solvent used, are Day-Glo A and AX Series pigments, the Radiant R-105 and R-106 Series, and Dane A and E Series pigments. These products are useful for A-type gravure where aliphatic and small amounts of aromatic solvents are used.

In C- and T-type gravure systems where oxygenated and aromatic solvents are used, the Radiant P-1700 Series and Day-Glo GT and STX pigments are recommended. A typical formulation for an A-type gravure ink is 30% Acryloid NAD-10 (Rohm & Haas), 50% fluorescent pigment, 5% toluene, and 15% heptane (as thinner).

8.4. Flexographic Inks

Fluorescent toners such as the Radiant GF, Lawter HVT, and Day-Glo HM and HMS Series toners are used in flexographic ink formulations. These products are soluble in blends of alcohol (80%) and ester solvents (20%) and are compatible with modifying materials such as nitrocellulose resins and acrylic solution polymers. Flexographic inks of this type are used most commonly to print products such as cellophane and polyethylene film for packaging, and also to print paper products such as gift wrap and price labels.

Water-based flexo inks can be formulated with either a soluble toner or with the Day-Glo EPX Series which is a true pigment and can be formulated like a conventional pigment dispersion. The Radiant Aquabest or the Day-Glo WST can be formulated in an alkaline water-soluble system to yield strong inks. They have limited shelf life and inferior fade, but do not necessarily require additional binder. Day-Glo EPX must be formulated with a binder such as a hard resin or can be used with one of the soluble toners such as WST. The EPX Series has several advantages over soluble toners such as much superior fade, excellent ink stability, and some hiding power over kraft-type papers. A disadvantage of the EPX is its lower tinctorial strength than other fluorescent toners.

8.5. Screen Inks

Among the earliest uses for products containing daylight-fluorescent pigment was screen printing inks. The process involves pushing ink through a coarse screen leaving a heavy deposit. This process is used to make outdoor and point of purchase advertising. By using daylight-fluorescent pigments in the ink, previously unattainable brilliance was achieved which provided longer viewing hours, particularly under low light conditions, such as at dawn, dusk, and on cloudy days.

This remains a good market for fluorescent pigments for the same reasons, and many boards have been fitted with ultraviolet lights or filtered white light to further increase the impact and extend the viewing time through the nighttime hours. Lawter B-3500 Series, Day-Glo A and AX Series pigments, and Radiant R-105 and R-106 Series are recommended. Formulations for screen ink employ complex vehicles and about 35% pigment.

8.6. Lithographic and Letterpress Printing Inks

Fluorescent pigments of fine enough particle size for litho and letterpress printing inks could not be obtained by standard techniques when starting with dry pigment. However, manufacturing spherical fluorescent particles *in situ* in a paste-ink vehicle made acceptable printing properties possible. Typical products include Day-Glo Starfire Series printing-ink bases, Radiant VF and Visiprint Series printing-ink bases, and Dane OLC Series bases. These bases are similar in nature to one another, although modifications of the ink formulation are needed depending on the specific product. The following is a typical finished formulation for a fluorescent lithographic ink starting with one of the above-mentioned printing-ink bases. Certain types of driers accelerate drying but may cause darkening of the ink, such as cobalt driers.

8.7. Vinyl Products

The use of fluorescent colorants in vinyl products, especially calendered and cast films, has opened up another important market. Because of the thickness of vinyl sheeting and cast articles, excellent exterior durability can be achieved. In Europe there is a very large market for fluorescent vinyl film for safety marking and

Component	Wt %
fluorescent-ink base	84.0
polyethylene wax compound	6.0
gloss varnish (tung oil-based)	3.6
tridecyl alcohol	4.2
driers	2.0
antioxidant	0.2
Total	*100.0*

high visibility applications such as on emergency vehicles and construction equipment, and there is a growing market in the United States and Asia.

For vinyl plastisol, organosol products and calendering, Day-Glo Color Corp. offers T, D, VC, and AX-Series pigments, Lawter Chemical offers the B-3500 and G-3000 Series, and Radiant Color offers P-1600 and R-203-G Series. In addition, Day-Glo offers VC Series for vinyl calendering where nonformaldehyde products are needed.

9. Health and Safety Factors

Good safety practices are recommended when handling fluorescent pigments, including a respirator and dust collecting equipment. The pigments present no unusual fire or explosion hazards. They clean up easily with detergent and water or solvents appropriate for the coating vehicle system.

Daylight fluorescent pigments (qv) are considered to be nontoxic. Since they are combinations of polymers and dyestuffs, the combined effect of the ingredients must be taken into account when considering the net toxic effect of these materials. Table 5 gives results of laboratory animal toxicity tests of standard modified melamine–formaldehyde-type pigments, the Day-Glo A Series, and the products recommended for plastic molding, Day-Glo Z-series.

Table 5. Results of Laboratory Animal Toxicity Tests

Test	Day-Glo A-Series	Day-Glo Z-Series
acute oral toxicity LD_{50}, g/kg	16.0	15.38
acute dermal toxicity LD_{50}, g/kg	23.0	3.0
acute dust inhalation LC_{50}, mg/L air	4.4[a]	2.88
eye irritation	no significant	mildly irritating

[a] Four hours.

In heavy-metal analysis of the same pigments, metals found were present in only trace amounts. The data listed place the products tested in the category of nontoxic materials. The Radiant Color Co. has conducted toxicity tests on its own products similar to the A-Series and has found them to be nontoxic. Heavy metals were found only in trace amounts in these tests.

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