Introduction to the Colour Index:
Classification System and Terminology

1. Introduction

Colour Index Classification ~ Overview

The Colour Index uses a dual classification system. The prime descriptor, in that it is the one most commonly used in discussions by colorant users and is the one easier to remember, is the *Colour Index Generic Name* (often abbreviated to CIGN). The other descriptor is the *Colour Index Constitution Number* (often abbreviated to CICN) which is chemical-structure related.

Definition of a Colour Index Generic Name

A **C.I. Generic Name** describes a commercial product by its recognised usage class, its hue and a serial number (which simply reflects the chronological order in which related colorant types have been registered with the Colour Index), e.g. C.I. Acid Blue 52, C.I. Direct Red 122, C.I. Pigment Yellow 176 and C.I. Solvent Black 34.

This definition enables a particular commercial product to be classified along with other products whose **essential colorant** is of the **same chemical constitution** and in which that essential colorant results from a single chemical reaction or a series of reactions. *The definition also includes multi-constituent substance or 'products by process'* [see e.g. Regulation (EC) No 1907/200 REACH and related RIPS]. *It is intended to exclude products obtained simply by physical admixture of essential colorants*.

In some cases, the same essential colorant is present in more than one application category. Typically, a disperse dye can often be applied as a solvent dye, and a vat dye can sometimes be used as a pigment.

However, it cannot be guaranteed that the essential colorant of each and every C.I. Generic Name results from a single chemical reaction or series of reactions and that there are no physical admixtures. The Colour Index is a living document and has had to adapt to advances in analytical techniques and the additional information now requested from registrants. Consequently, that which was acceptable historically is now viewed more critically.

Many commercial products contain, as well as the substance responsible for the colour, quantities of other chemicals (generally referred to as *additives*) designed to improve the application properties of the product, such as the dispersibility, flow and flocculation resistance of pigments; dyes often contain significant amounts of diluents. In all cases, **the essential colorant is the portion of the material responsible for the colour** and excludes any additives.

Colorants listed under a C.I. Generic Name whose serial number contains a **colon** differ slightly from those listed under the parent C.I. Generic Name. This slight difference is usually chemical but may be due to different crystal modifications in the case of certain pigments.

Historically, a colon number was added to the serial number of a particular C.I. Generic Name when a new product was reported by a manufacturer as being *similar to* the original. 'Similar to' can generally be interpreted as meaning slightly different chemically. This imprecise definition gave manufacturers the opportunity to request new C.I. Generic Names for products that should have been given colon numbers. Conversely, subsequent disclosures revealed that certain products that had been given colon numbers should really have been allocated new generic names. The system has, nevertheless, been continued where it was considered helpful to users to group certain colorants together in this way.

C.I. Constitution Numbers

Where the chemical constitution of an essential colorant has been disclosed for publication, it has been classified and allocated a separate five-figure C.I. Constitution Number; since 1997, new disclosures have been allocated six-figure C.I. Constitution Numbers to alleviate the congestion experienced in certain areas, notably monoazo colorants. In each category, the various colorants are arranged strictly on the basis of their chemical structures.

In Volume 4 of the Third Edition of the Colour Index, published in 1971, it was pointed out that ***where dyes or pigments differ only in the metal or acid used for salt formation, a subdivision has been made by addition of a sixth figure after a colon*** (currently, a seventh figure after a colon). Thus, for example, C.I. Pigment Red 48 (C.I. 15865) is the sodium salt and C.I. Pigment Red 48:1 (C.I. 15865:1) is the barium salt. It should be noted, however, that colon numbers attached to particular generic names do not necessarily coincide with those attached to the corresponding constitution numbers. Also, colon numbers associated with a particular structure may relate to quite different generic names. For example, C.I. 42535 (C.I. Basic Violet 1) is the chloride salt, C.I. 42535:1 (C.I. Solvent Violet 8) is the free base, C.I. 42535:2 (C.I. Pigment Violet 3) is the phosphotungstomolybdic acid salt and C.I. 42535:3 (C.I. Pigment Violet 27) is the copper ferrocyanide salt.

The use of colon numbers has been extended, somewhat arbitrarily, to include small structural differences (e.g. C_2H_5 instead of CH_3 or Br rather than Cl); this kind of use is best avoided. The advent of six-figure C.I. Constitution Numbers made it possible to minimise the use of colon numbers.

Colon numbers have also been used to distinguish between analogues of metal phthalocyanines and to cover relatively minor variations in composition in the case of some inorganic pigments.

Allocation of a new Colour Index Generic Name (Current Procedure)

The allocation of a new C.I. Generic Name is made in response to a specific request from the manufacturer of the new commercial product.

A new C.I. Generic Name (e.g. C.I. Pigment Yellow 220) for inclusion in the **Colour Index International Fourth Edition On Line** is allocated following the receipt of a valid Product Registration Form (supplied by the Society of Dyers and Colourists). As well as providing standard information, such as recommended end uses, the manufacturer also has the opportunity to highlight any special features of the product.

In order to minimise the possibility of duplication, the chemical structure of the essential colorant has to be disclosed but will be kept confidential if so desired. The manufacturer has to provide a signed declaration that, to the best of his knowledge, all the information supplied is correct.

2. Colon Numbers and Organic Pigments

Background

As pointed out in the introduction, so-called 'colon numbers' have been used in the Colour Index to subdivide both C.I. Generic Names and C.I. Constitution Numbers in order to distinguish minor differences in properties or structure. Unfortunately, no rules have ever been published and consequently the use of colon numbers has not been consistent.

A specific example of the use of colon numbers occurs with the metal-complex phthalocyanine pigments C.I. Pigment Blue 15 (C.I. 74160) and C.I. Pigment Blue 75 (C.I. 74160:2) where the only structural difference is a change of metal from copper to cobalt.

In the organic pigments sections, the use of colon numbers has mainly been adopted to distinguish between various toner pigments ('lakes' in US terminology) and to distinguish pigments where crystal modification causes products with the same chemical structure to have significantly different colours and/or properties.

Although previous usage has been inconsistent, there is no suggestion that it would be desirable to change existing designations, as this would cause confusion and could additionally affect, for example, the registration status or food-contact status of commercial products. Therefore, in an effort to prevent further inconsistencies occurring, the following rules have been adopted after consultation with industry. It is hoped that they will prove acceptable on both technical and commercial grounds.

Toners

Although in the USA the term 'toner' is used for all organic pigments, in the EU it is reserved for pigments that are made by synthesising an insoluble salt of a dye. If the dye is an anionic (or acid) dye, this is achieved by reacting the soluble acid dye with a water-soluble metal salt, such as barium, calcium, manganese, etc. In the case of cationic (basic) dyes, the insolubilising group has to be a complex acid, such as phosphotungstomolybdic acid (PTMA). In the organic pigment sections of the Colour Index, colon numbers have been used to distinguish between the various counter-ions used in these colorants.

In order to avoid possible confusion, anionic toners will be referred to as *anionic organic pigments* and, similarly, cationic toners will be referred to as *cationic organic pigments*.

Anionic organic pigments

When a new anionic organic pigment is registered for which no C.I. Generic Name or C.I. Constitution Number already exists, the parent structure will be given a C.I. Constitution Number without a colon. A C.I. Generic Name will only be appropriate if there is a commercial product, which could be either a dye (which may already be listed as such in the Colour Index) or a new colorant. Neither alternative will have a pre-existing C.I. Pigment (e.g. Red) designation. The first commercial pigment to be registered, with the Colour Index, which is derived from the parent structure will be given a C.I. Generic Name ending with ':1' and the chemical constitution will have the same colon number (i.e. in this case ':1'). Subsequent introductions using other counter-ions will carry colon numbers in numerical order of registration.

For example, consider the introduction of a new red anionic organic pigment where the parent structure is given the Constitution Number C.I. 888800. As C.I. 888800 does not represent a commercial product, there is no associated C.I. Generic Name. If the calcium salt is the first commercial pigment to be registered, this would be, say, C.I. Pigment Red 1000:1 and its C.I. Constitution Number would be C.I. 888800:1. Subsequently, if, say, the manganese salt were to be introduced, this would then be designated C.I. Pigment Red 1000:2 with C.I. Constitution Number C.I. 888800:2, and so on for any further counter-ions.

Occasionally, anionic organic pigments can have two associated counter-ions present, both singly and in combination. This situation would be recognised by assigning three C.I. Constitution Numbers (each with a different colon number). A third C.I. Generic Name, associated with the product having both counter-ions present, would only be justified, however, if the properties of the resulting pigment were significantly different from those of the corresponding physical mixture, and there was additional physico-chemical evidence to suggest differences in the crystal structure.

Cationic organic pigments

The situation is similar to that obtaining with anionic organic pigments. However, when copper(I) hexacyanoferrate(II) acid has been used as the precipitating acid, the resulting pigments have in the

past been given a different generic name. For example, the so-called 'copper ferrocyanide' pigment corresponding to the various C.I. Pigment Red 81 types is C.I. Pigment Red 169 (C.I. 45160:2).

This distinction will be preserved. Thus, when copper(I) hexacyanoferrate(II) acid is used as the precipitating acid, the commercial pigments will therefore be given a different C.I. Generic Name. Historically, the same C.I. Generic Name (with different colon numbers) has sometimes been allocated to cationic dyes which have very similar, but not identical, structures (e.g. methyl versus ethyl ester groups). In future, the Colour Index will only allocate the same C.I. Generic Name (with different colon numbers as necessary) when the same cationic dye is used.

Crystal modifications

The classic example of a pigment having different names for the various crystal modifications is phthalocyanine blue, which has been classified as C.I. Pigment Blue 15. C.I. Pigment Blue 15:1, which is reddish-blue, is the α-modification while C.I. Pigment Blue 15:3, which is greenish-blue, is the β-modification. These products carry the same C.I. Constitution Number: C.I. 74160.

In contrast, C.I. Pigment Blue 15:2 and C.I. Pigment Blue 15:4 are, respectively, α- and β-modifications which have been given an after-treatment to make them flocculation stable. In fact, most commercial phthalocyanine pigments are after-treated, so this is another example of lack of consistency in past Colour Index practice as regards the allocation of colon numbers. The division between C.I. Pigment Blue 15:1 and Blue 15:2, and between C.I. Pigment Blue 15:3 and Blue 15:4, is becoming increasingly blurred. Although this anomaly is recognised, it is not the intention that it will become a precedent for any other chemical types introduced in the future.

The industry's understanding of the role of crystal structure and particle-size effects is growing, and it is now acknowledged that several pigments can exist in more than one crystal form, each of which, with any given pigment, is chemically identical. In assigning C.I. Generic Names and C.I. Constitution Numbers, the Colour Index has usually ignored small differences in colour or properties. However, in some cases different crystal forms of a pigment exist in different colours. An example is C.I. Pigment Violet 19, which can exist as a violet pigment and also as a bright red. In such cases it is possible to apply for a new C.I. Generic Name in order to distinguish between the two types.

Sometimes different crystal forms of a pigment exist in the same sector of the spectrum, although showing very noticeable differences in hue or even properties. If the difference is great enough to change the description of the hue (e.g. yellowish red to bluish red), then a new colon number would be considered for an existing C.I. Generic Name.

3. Colon Numbers and Solvent Dyes

Background

In the solvent dyes sections of the Colour Index, the use of colon numbers has mainly been adopted to distinguish between the different salts of various azo metal-complex dyes. Other occasional usage relates to the free bases of some cationic dyes and to groups of structurally very similar dyes.

Azo metal-complex dyes

Improved solubility in non-aqueous solvents can be achieved by forming amine (e.g. 2-ethylhexylamine) salts of azo metal-complex dyes. In such cases, the parent (usually sodium) salt may have a pre-existing C.I. Solvent (e.g. Red) designation. The alkylammonium salt of the azo metal-complex solvent dye will be given the same C.I. Generic Name ending with ':1' and the chemical constitution will be allocated an appropriate six-figure number. Any subsequent products involving different amines will carry colon numbers in numerical order of registration.

Most 1:2 metal-complex dyes are formed by reacting an appropriately-substituted monoazo dye with a metal (usually chromium or cobalt) salt. Occasionally, two different monoazo dyes are used, giving rise to an AA, BB, AB mixture (by process) of three 1:2 metal-complex dyes. In such a situation, each (new) component will be assigned a six-figure C.I. Constitution Number and the mixed product will be given a C.I. Generic Name. It has to be recognised that the AA and BB components may have pre-existing C.I. Generic Names and C.I. Constitution Numbers, possibly including colon numbers.

Free bases of cationic dyes

The free bases of some cationic dyes are used as solvent dyes. In the case of the classic triarylmethane and xanthene colorants, the C.I. Generic Name of the related solvent dye does not include a colon number, unlike the corresponding C.I. Constitution Number which usually, but not always, terminates with ':1'. A typical example is C.I. Solvent Red 49 (C.I. 45170:1). The registration of a new solvent dye based on an existing, or a novel, basic dye structure would be dealt with similarly.

Closely-related dye structures

Close similarities between the structures of several commercial products can justify the allocation of colon numbers, particularly when the manufacturers involved need to distinguish between the different products. The disazo dyes C.I. Solvent Red 164, C.I. Solvent Red 164:1 and C.I. Solvent Red 164:2 provide such an example. The structures of the dyes involved are confidential but an appropriate six-figure C.I. Constitution Number has been allocated in each case.

In a manner similar to azo metal-complex dyes, solubility in non-aqueous solvents can be achieved with phthalocyanine derivatives by using appropriate amines. For example, treatment of C.I. Direct

Blue 86 (C.I. 74180) with 2-ethyl-*N*-(2-ethylhexyl)-1-hexanamine gives C.I. Solvent Blue 129 (C.I. 74180:2); the barium salt (C.I. 74180:1) is C.I. Pigment Blue 17. In these cases, the same chromophore is involved but the application properties are different, as determined by the substituents present in the parent structure.

These examples illustrate how colon numbers have been used to distinguish small differences in properties or structure. In future, (new) similar chemical structures will be allocated appropriate six-figure C.I. Constitution Numbers without colons.

4. Colon Numbers and Inorganic Pigments

Background and future

Relatively few colon numbers have been issued in the inorganic pigments section of the Colour Index. In the case of some extended pigments obtained by a process of co-precipitation, or physical admixture, both the C.I. Generic Name and the corresponding C.I. Constitution Number have been allocated ':1'. A typical example is the cadmium sulfide pigment C.I. Pigment Yellow 37 (C.I. 77199) which, when co-precipitated or admixed with with barium sulfate, results in C.I. Pigment Yellow 37:1 (C.I. 77199:1).

Other limited usage has been varied and somewhat inconsistent. For example, C.I. Pigment White 18 (C.I. 77220) covers synthetic calcium carbonate and naturally occurring materials such as chalk, limestone and marble. C.I. Pigment White 18:1 (C.I. 77220:1) represents the naturally occurring mineral dolomite, consisting of calcium magnesium carbonate. Different crystal forms of cerium(III) sulfide (Ce_2S_3) result in C.I. Pigment Orange 75 (C.I. 77283:1) and C.I. Pigment Red 265 (C.I. 77283:2). In another example, C.I. Pigment Blue 36 (C.I. 77343) is derived from the oxides of cobalt, aluminium and chromium whereas the formation of C.I. Pigment Blue 36:1 (C.I. 77343:1) also involves zinc oxide. Similarly, C.I. Pigment Green 52 (C.I. 77437:1) is derived from the oxides of copper and silicon whereas C.I. Pigment Blue 31 (C.I. 77437) results when calcium is also involved.

These examples illustrate how colon numbers have been used to distinguish differences in properties or structure. There is no intention of introducing any new colon number usage into the inorganic pigments section.

5. Summary

All colon numbers previously assigned will be retained but it is anticipated that in future new colon numbers will only be available for:

- anionic and cationic organic pigments
- crystal modifications
- azo metal-complex dyes
- free bases of cationic dyes
- closely-related dye structures
- co-precipitated inorganic pigments

Except for the variable salts of anionic and cationic dyes and pigments, and for azo metal-complex dyes, it is intended that, as far as possible, each newly disclosed chemical constitution will be allocated a six-figure C.I. Constitution Number without a colon.

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