Eurocolour

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Guidance document for the Registration of CICPs

Table of contents

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1. Introduction

Complex Inorganic Colored Pigments (CICPs) are chemical substances manufactured by means of an industrial process, which involves a chemical reaction. In this process, a mixture of raw materials (typically consisting of metal oxides and salts) undergoes a calcination reaction at high temperatures forming a specific crystalline matrix.

For the identification of CICPs, color and crystal structure have been widely used as main parameters by industry. The Color Pigment Manufacturers Association (CPMA) maintains a list of inorganic pigments grouped into 14 crystalline structures with different contributing elements and colors. Colour Index International is a reference database listing thousands of dyes and pigments either organic or inorganic describing a commercial product by usage, its hue and a serial number.

The purpose of this document is to guide potential registrants of CICPs in determining the substance identity of these complex substances for the Registration under the REACH Regulation[1]. The criteria used to define the boundaries of what is considered the same substance under REACH affects the number of substances that will be registered jointly and defines the corresponding obligations to generate relevant Annex VII-XI data.

2. REACH Substance Identification

REACH Regulation distinguishes the following types of substances for the purpose of Substance Identification:

- Mono-constituent substances in which one constituent is present at a concentration of at least 80% (w/w).
- Multi-constituent substances consisting of several main constituents present at concentrations generally above or equal to 10% and below 80% (w/w).
- Substances of unknown or variable composition, complex reaction products, or biological materials (UVCBs).

In the past, CICPs have been considered as mono-constituent substances using the CPMA nomenclature, including CAS and EINECS numbers, for the joint REACH Registrations. This approach encountered certain issues with Substance Identification under REACH, mainly due to the variability of the compositions within the same CICP.

The CPMA entries allow for so-called color modifiers, which may be incorporated into a CICP without any restrictions as long as the crystal structure is unchanged. In addition, a mineralizer may be used to control pigment formation by facilitating crystal growth. Consequently, CICPs with significantly different compositions had been registered jointly with the same name and Substance Identity. For this reason, REACH registrations using the CPMA nomenclature came

[1] *Regulation (EC) No 1907/2006 of the European Parliament and of the Council of 18 December 2006 concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals.*

under scrutiny due to some inconsistences identified by ECHA with the substance identification rules defined in the REACH legal text and ECHA Guidance documents.

One option might be to consider CICPs as UVCBs, which allows for variations in composition. Subsequently following the Guidance for identification and naming of substances under REACH and CLP, UVCBs should be identified as a combination of composition, source (raw materials) and manufacturing process.
These parameters are however not relevant for CICPs, because a single CICP can be manufactured using a variety of raw materials or different industrial conditions. In addition, the concept of impurities, which does not apply to UVCBs, is relevant for CICPs.

So, neither the identification as mono-constituent substances nor as UVCBs will allow for the necessary derogations from the strict principles for naming substances under REACH and CLP. A minimal variation in composition, impurity concentration, type of raw material or processing conditions would trigger a separate REACH Registration, which would result in a disproportionate burden especially to small and medium-sized enterprises manufacturing CICPs. The aim of the present guidelines is to overcome these challenges and set specific rules for substance identification of CICPs under the principles of REACH Regulation.

3. Naming and Substance Identification of CICPs under REACH – Key parameters

X-ray fluorescence (XRF), and Inductively Coupled Plasma (ICP) for metals are widely used for the chemical analysis of CICP. The chemical composition is of prime importance for Substance Identification under REACH. In addition to composition, the crystalline structure is a very relevant parameter, which is investigated by X-ray Diffraction (XRD) and can be quantified using the Rietveld method. Scientific studies of the crystalline structure use these techniques extensively.

For Substance Identification and naming under REACH, a CICP therefore will be identified by these two key parameters: its crystal structure and chemical composition.

The so-called 80%-10% rule is the basis for the nomenclature of CICPs under REACH. More specifically, the basic rules to name CICPs under REACH and CLP are the following:

- Main contributing elements always present in the name
- Name of element (e.g. aluminium, chromium) instead of metal speciation (aluminate, chromite)
- Crystalline structure (e.g. spinel, rutile) included at the end of the name as a general rule (see section 3.2)

Colour does not need to be mentioned in the name. Nevertheless, if the existing EC name follows all the previous basic rules and includes the colour, a modification of the EC name is not required.

3.1. Chemical composition of CICPs

Chemical composition of CICPs is usually expressed as oxides (as a result of the XRF or ICP analysis), even if the metal oxides are used as raw materials and they are completely transformed during the pigment manufacture.

The so-called 80%-10% rule is the basis for the nomenclature of CICPs under REACH. According to their chemical composition, this means that all main contributing elements are always present in the name**.** As a general rule, main contributing elements are all those present at a concentration of 10% or higher (expressed as oxides). However, there can be exceptions to this rule. This concept is further developed in the following sections.

3.1.1. Main contributing elements present in concentration above 10 %

As a general rule, all contributing elements above a concentration of 10% (expressed as oxides) are considered as main elements and will contribute to the name. The sum of all main elements (expressed as oxides) must add to more than 80% of the substance.

The following examples of the so-called 80%-10% rule illustrate the naming principle:

- A spinel with more than 80% (w/w) cobalt and chromium oxides combined, and less than 10% (w/w) aluminium oxide is named “Cobalt chromium spinel”.

- A spinel with cobalt and chromium oxides, containing also aluminium oxide in a concentration above 10% (w/w), and more than 80% (w/w) all combined, is named “Cobalt chromium aluminium spinel”

Nevertheless, there are cases where some flexibility to the 80-10% rule is needed, for example where a contributing element always represents 8-12% of a given pigment. In this case, all the compositions of the same CICPs should be registered jointly (see section 3.1.2, Case B).

3.1.2 Flexible application of the so called 80%-10% rule

Case A) Main contributing elements present in concentration below 10 %

Certain elements may be always present in concentrations below 10% while being color-determining, therefore necessary for the identification of a given substance. In these cases, such contributing elements need to be present in the name of the pigment for a proper identification.

For example, praseodymium or vanadium oxides are always present in concentrations below 10% in certain zircon pigments. Yet they are main elements, important to define the yellow or blue color of the substances. If the 80-10% rule was to be strictly followed, these pigments would be included in the same Registration dossier and considered as the same substance (zirconium zircon). However, they are different substances for the colour industry. Additional examples are nickel, chromium and antimony oxide in rutile pigments, chromium oxide in sphene pigments, or vanadium oxide in pigments with baddeleyite structure. Table 1 shows the pigments impacted by this specific deviation, and their substance names including also the main elements present below 10% (w/w).

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Table 1 CICPs containing main elements below 10% (w/w)

Concentration of the main contributing element	80%-10% rule strictly applied	Substance name with all main elements, including those <10%(w/w)
2%≤ CdO ≤8%, 0.5% S+Se ≤5%	Zirconium zircon	Zirconium zircon with encapsulated cadmium selenium sulphide (EC# 701-413-5)
2%≤ CdO ≤6%, 0.5%≤S ≤5%	Zirconium zircon	Zirconium zircon with encapsulated cadmium sulphide (EC# 701-446-5)
2%≤ Pr4O11≤9%	Zirconium zircon	Zirconium praseodymium yellow zircon (EC# 269-075-7)
1%≤ V2O5 ≤5%	Zirconium zircon	Zirconium vanadium blue zircon (EC# 269-057-9)
2%≤ NiO ≤8%	Antimony titanium rutile	Antimony nickel titanium rutile (EC# 701-459-6)
0.3≤ Cr2O3 ≤5 %	Tin orchid cassiterite	Chrome tin orchid cassiterite (EC# 269-104-3)
0.3≤ Cr2O3 ≤3%	Tin calcium silicon sphene	Chromium tin calcium silicon sphene (269-073-6)
0.5%≤ V2O5 ≤5%	Zirconium baddeleyite	Vanadium zirconium yellow baddeleyite (269-063-1)

Case B) Flexibility of the 80-10% rule for borderline cases

In certain cases, the strict application of the 80%-10% rule with respect to the chemical composition would lead to a situation where additional Registration dossiers would be required, because of minor contributing elements not being colour-determining and present in concentrations very close to 10%.

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Table 2 illustrates examples of this situation and the reported percentages of these “borderline elements”.

Table 2. CICPs containing elements in concentrations very close to the limit of 10% (w/w)

		Substance name	
		Rule 80-10% strictly applied	**Flexibility of 80-10% rule**
Zinc iron chromite brown spinel EC 269-050-0 CAS 68186-88-9 Colour Index 77503	**Company A** reports zinc, iron & chromium oxides as main contributing elements	Zinc iron chromium spinel	Zinc iron chromium spinel
	Company B reports zinc, iron, chromium & aluminium oxides as main contributing elements	Zinc iron chromium aluminium spinel	Zinc iron chromium aluminium spinel
	Company C reports zinc, iron, chromium & aluminium oxides as main contributing elements, plus NiO≤11%	Zinc iron chromium aluminium nickel spinel	
	Company D reports zinc, iron, chromium & aluminium oxides as main contributing elements, plus SiO_2≤12%	Zinc iron chromium aluminium silicon spinel	
	Company E reports zinc, iron, chromium & aluminium oxides as main contributing elements, plus NiO≤11% and SiO_2≤12%	Zinc iron chromium aluminium nickel silicon spinel	
Number of REACH Registration Dossiers		5	2

In this and few other cases, the limit could be up to 12% (w/w) to avoid an excessive burden to industry and unjustified multiplication of Registration dossiers with minimal changes in compositions. It would prevent a potential situation where a registrant whose composition contains 9% of a given element needs to prepare a different Registration dossier than another registrant whose composition contains 11% of the same element.

Case C) Main contributing elements present either above or below the cutoff value of 10% (w/w)

In cases where a main contributing element is present either in less or more than 10% (w/w) (depending on the specific composition) these compositions should be included in the same Registration dossier. The main elements are always present in the name of the substance, be it below or above 10%. This would be the case in the following examples:

- Chrome tungsten titanium buff rutile (EC# 269-054-2) — 5%≤ Cr_2O_3 ≤15%
- Manganese antimony titanium buff rutile (EC# 270-185-2) — 8%≤ MnO ≤15%
- Tin antimony cassiterite (EC# 269-105-9) — 2%≤ Sb_2O_3 ≤12%
- Chrome antinomy titanium buff rutile (EC# 269-052-1) — 2%≤ Cr_2O_3 ≤13%
- Manganese aluminia pink corundum (EC#269-061-0) — 0.5%≤ MnO ≤17%

Case D) Contributing elements not required in the substance name.

Silicon is a necessary element for the formation on crystalline structures such as zircon and olivine. As such, it is implied in the crystalline structure mentioned in the substance name. For that reason, in complex inorganic pigments with a structure of zircon or olivine it is not necessary to include the name if the element silicon in the substance name, even if it is a main element.

3.2 Crystalline structure of CICPs

Together with chemical composition, crystalline structure is a key defining parameter of the substance identify of CICPs. As a general rule, the crystalline structure of CICPs is included at the end of the name (zircon, rutile, spinel, baddeleyite, etc).

3.2.1 Accepted deviations from the general rule

Case A. Crystalline phase is already included in the existing EC name but not at the end, and all the main constituents are also mentioned in the name, as in the following substances:

- Spinels, chromium iron manganese brown (271-411-2)
- Pyrochlore, antimony lead yellow (EC# 232-382-1)
- Olivine, cobalt silicate blue (EC# 269-093-5)

Case B. Crystalline structure is not mentioned in the EC name, but all main elements are listed in the name and their crystal structure can be implied from their composition, as in the following substances:

- Chromium iron oxide (EC# 235-790-8)
- Diiron magnesium tetraoxide (EC# 235-107-3)

3.2.2 CICPs containing multiple crystalline structures

Some complex inorganic pigments contain more than one crystalline structure. The fraction of each crystalline structure can be quantified via the Rietveld analytical method.

Case A. Different phases with the same elemental composition.

When different phases with the same elemental composition are present, they can be registered in a single joint submission, but this is not acceptable if their chemical composition is different.

As an example, different crystal phases of TiO_2 where one composition is pure rutile and another is anatase or a mix of anatase and rutile can be registered in a single joint submission. However, a composition covering anatase and another one covering anatase and potassium titanate (both above 10%), could not be registered in a single joint submission.

Case B. Different phases with different elemental composition and main crystalline phase always present ≥80% w/w.

When different phases with different elemental composition are present, if the main crystalline phase is present is always present ≥80% w/w, the substance EC name should only include the main crystalline structure. Secondary phases do not need to be included in the substance name.

It is acceptable to register compositions with a crystal phase ≥80% and secondary phases ≤20% as the same substance, as long as:

- It is transparently communicated in the compositions section of the REACH dossier and minor phases are identified with their structure and chemical identity, e.g. if the minor phase is SiO_2 in the form of quartz, cristobalite and/or tridimite or a combination of them, it must be specified when reporting the composition.

- The data provided to fulfil the REACH requirements is representative of all compositions covered by the joint submission.

Example 1: a substance with a main crystalline phase of spinel >80% w/w and a secondary phase of corundum <20% w/w can be registered as a single phase substance with only spinel in the substance name.

Case C. Different phases with different elemental composition in concentrations between <80% and ≥10% w/w

When different phases with different elemental composition are present in a concentration <80% and ≥10% w/w, all of them should be included in the substance name.

If a sample of a certain substance has a main crystal phase ≥80% w/w and another sample has a main phase <80% w/w and secondary phases ≥10% w/w, two different registration dossiers are needed: one covering the compositions with the main phase always present ≥80% w/w and another covering the compositions with the main phase always <80% w/w and a secondary phase always ≥10% w/w. The deviation from the 80/10% rule is applicable for borderline situations (e.g. 79%).

Example 2: a pigment with a main phase of spinel at 70% and a secondary phase of corundum present at 20% cannot be registered together with the substance from Example 1 above. It needs to be registered as a different substance, identified with the name of its main constituents plus the structure names spinel and corundum.

3.2.3. CICPs containing encapsulated crystal structures

Certain complex inorganic pigments contain a secondary crystalline structure encapsulated within a matrix of zircon. In such cases, the substance name must specify the encapsulation, regardless of the concentration of the encapsulated structure.

Examples:

- Zirconium zircon with encapsulated hematite
- Zirconium zircon with encapsulated cadmium sulphide
- Zirconium zircon with encapsulated cadmium selenium sulphide

4. Use of boundary composition

As outlined above, CICPs are composed of main and minor contributing elements.

The Lead Registrant dossier must report the boundary composition on behalf of all members of the joint submission. For a CICP, the boundary composition is defined by the crystal structure(s) and

- the main contributing elements, expressed as the list of the respective oxides in a certain range covering all the compositions of all registrants in the joint submission
- the minor contributing elements present < 10 % (so-called color modifiers).

The boundary composition maintained by the Lead Registrant as agreed in the SIEF and reported in the Lead Dossier does not necessarily contain all minor contributing elements, since some of them may be specific to a single co-registrant.

It is the responsibility of the individual registrants to maintain the composition for their respective legal entities in their individual REACH dossier, listing all minor contributing

elements not included in the boundary composition as well as impurities. As a consequence, the individual registrants need to assess whether their individual compositions are adequately covered by the joint chemical safety assessment. If the hazard profile of the dossier is not affected, the lead registrant will update the boundary compositions upon request from the individual registrant.

If this is not the case (because of minor element(s) triggering a different hazard profile), the concerned company will have the possibility to opt-out for the relevant part of the joint dossier and conduct its own specific chemical safety assessment.

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About Eurocolour:
Eurocolour e. V. is the umbrella association for manufacturers of pigments, dyes, fillers, frits, ceramic and glass colours, and ceramic glazes in Europe.