

Effects of Impending EU Regulations on the Search for "Safe" CIJ Inks

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Abstract

Upcoming changes to EU regulations are likely to have a major impact on the hazard classification and labeling of industrial continuous ink jet (i-CIJ) inks.

The requirements for an ideal i-CIJ solvent are discussed from a physical properties, health, safety and environmental (HS&E) perspective, with reference to both traditional and more recently introduced solvents, and to the use of water. The effects of two major EU Directives are then discussed. Firstly, the 25th Adaptation to the Dangerous Substances Directive assigns additional risk phrases and hazard symbols to a range of solvents used by the industry. Examples of the effects are given. Secondly, the new Preparations Directive introduces the requirement for the environmental classification of preparations. The criteria forcing use of the N symbol are outlined and examples using dyestuffs are given.

Other recent EU legislation is briefly summarized, and future trends in the use of solvent-based i-CIJ inks will be postulated.

Introduction

The EU and the USA form two of the major regulatory regions in the world. Both areas have introduced a wide range of legislation covering the use of chemicals by industry, with the aim of protecting workers, the general public and the environment. This paper looks at two major upcoming changes to EU Directives that will have a direct effect on many of the raw materials used in the manufacture of ink jet inks.

i-CIJ Inks[1]

Since its commercial inception in the 1970's, industrial continuous ink jet (i-CIJ) printing[2] has fulfilled the requirements of high volume manufacturers who wish to code their products with variable information, such as batch codes, sell by dates, sequential numbering, etc. The properties required of an ideal i-CIJ ink are daunting. It should have a fast drying time (~1 second), adhere to all types of porous and non-porous surface, be non-flammable and non-toxic, contain no VOCs, be stable for ≥1 year, be easily cleaned off the printer, and require no secondary cure processes. From an end user point of view, one of the most important factors is printer reliability. Users do not want expensive downtime on their production lines due to faulty CIJ printers. No one ink meets all these criteria; solvent based, water based, UV cure and other reactive systems will each give some but not all of the required properties. In practice, solvent-based i-CIJ inks are by far the most widely used, and for the purpose of simplicity, can be regarded as consisting of four types of raw materials - colorant (dye or pigment), binder, additive, and solvent.

Solvent Choice

If we now look at the critical properties required of a solvent for an i-CIJ ink, it quickly becomes clear which classes of solvent are most suitable (Table 1).

Table 1. Critical Solvent Properties for i-CIJ

	Solvency	Polarity	Volatility	HS&E
Ketones	***	***	***	*
Alcohols	***	***	**	**
Esters	**	**	***	*
Glycol Ethers	***	***	-	-
Ethers	*	*	***	-
Glycols	***	**	X	-
Chlorinated	***	**	***	X
CFCs	**	**	***	X
Aliphatic HC	X	X	***	X
Aromatic HC	X	X	*	X
Water	***	***	*	***

*** = excellent ** = good * = fair - = neutral X = poor

Polar oxygenated solvents such as ketones, alcohols and esters have the best mix of properties. Their main drawbacks of odor, flammability and HS&E profile (although the latter are relatively favorable compared to other solvent options) are outweighed by their positive features. Of course, within each solvent class individual solvents may be better or worse than their class average - careful choice is required to optimize the overall properties. Historically, methyl ethyl ketone (MEK), ethanol (EtOH) and methanol (MeOH) have been widely used; of those MEK has been and remains the dominant choice. Over the last 6 years acetone and ethyl acetate (EtOAc) have been introduced and their use is gradually increasing. Table 2 compares properties of these solvents.

Table 2. Physical Properties of i-CIJ Solvents

Property	MEK	EtOH	MeOH	Acetone	EtOAc	Water
Odor	Strong	Mild	Mild	Strong	Strong	None
Boiling Pt/°C	80	78	65	56	77	100
Flash Pt /°C	-7	13	10	-18	-2	-
Vapor Press[A]	77	43	96	185	73	17
Evapn. Rate[B]	5.7	3.3	4	11.5	6.2	0.4
Evapn. Time[C]	3.2	8.3	5.5	2.1	3	80
Conductivity[D]	20	N/A	100	15	0.2	114

[A] mmHg [B] butyl acetate = 1 [C] ethyl ether = 1 [D] µS/m

All these solvents are classified as hazardous for one reason or another and require precautions in their use. As such they are affected by the changing EU regulations, as we will see below. First however, it is clear that water is potentially a good solvent for CIJ. It is pertinent to discuss the use of water further.

Water as an i-CIJ Solvent

Water has all the properties to make a good CIJ ink from both a technical and a HS&E point of view. Unfortunately, its presence introduces problems in the printer and in application properties (Table 3).

Table 3. Pros and Cons of Water as an i-CIJ Solvent

PROS	CONS
Non-toxic	Foam generation
Non-flammable	Corrosion
No odor	Bacterial / fungal growth
Non-VOC	Restricted range of raw materials
Environmentally friendly	Fluctuations / instability due to pH variation
Instant customer acceptance	Dry time slow (>5 sec) and dependent on temperature and humidity
	Poor wetting on hydrophobic surfaces
	Variable adhesion
	Poor water resistance

It is important to note that an ink based on water may still be hazardous, due to the nature of the other raw materials used in the ink. These require careful choice to maintain the advantages of water whilst not compromising end user performance. Water based inks are also more likely to enter the aqueous environment, and as such may represent a greater pollution hazard. However, the obvious attractions of water based i-CIJ inks will continue to stimulate R&D aimed at overcoming the above obstacles to achieve the "Holy Grail", a fast drying water based ink with all the properties of today's MEK based inks.

EU Legislation

The EU has dual objectives of properly regulating the use of chemical substances and also of harmonizing minimum standards within its Member States. This will not necessarily achieve uniformity since in many cases Member States are allowed to establish or maintain more rigorous standards. EU legislation is proposed by the Commission of the European Communities (CEC) which currently operates through 24 Directorates General (DG) (note that these may be reorganized during 1999). The DG of most relevance for chemical legislation is DG11, whose responsibilities include Environment and Notification, Classification, Packaging and Labeling of Dangerous Substances and Preparations. Legislation requires approval by the Council of Ministers or a Technical Progress Committee, on which each Member State is represented. The legislation appears as Directives, which are binding on Member States and require incorporation into national legal systems. In the UK, chemical legislation is covered by the Chemicals (Hazard Information and Packaging for Supply) Regulations (CHIP).[3]

Dangerous Substances Directive (67/548/EEC)

As the name implies, this Directive applies to ***individual chemical substances***. Since it was first set out in 1967, the Directive has been subject to many "Amendments" and "Adaptations". The Directive lays down criteria against which a given chemical is judged, in order to determine whether it falls into any of the hazard categories defined by the legislation (covering physico-chemical, toxicological and ecotoxicological hazards). Classification is based on available experimental data. Hazard categories are identified by the use of a pictorial symbol, a letter and an indication of danger (Figure 1).

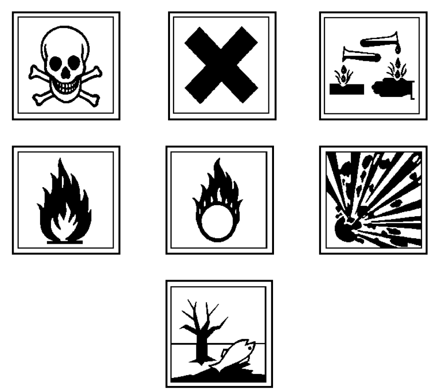

Figure 1. EU Hazard Symbols

All symbols are black on orange background. Top L to R: Toxic (T) or Very Toxic (T+); Harmful (Xn) or Irritant (Xi); Corrosive (C); Middle L to R: Highly (F) or Extremely (F+) Flammable; Oxidising (O); Explosive (E). Bottom: Dangerous for the Environment (N).

Risk (R) Phrases indicate the potential dangers of using the chemical, whilst Safety (S) Phrases provide brief summary advice to users on handling precautions. There are currently 65 Risk Phrases and 62 Safety Phrases. As an example, MEK is currently (1999) classified as F, Xi; R11 (Highly flammable), R36/37 (Irritating to eyes and respiratory system). This "headline" hazard information must appear on the container label and in the safety data sheet (SDS or MSDS).

Annex 1 of the Directive lists over 3000 of the most commonly used hazardous chemicals, with definitive classification symbols and Risk Phrases. It is important to note that for the vast number of chemicals not on this list, the onus is placed on suppliers to carry out self-classification of their product and provide correct labeling and SDS data.

The 25th Adaptation to the Dangerous Substances Directive (98/98/EC)

Released in December 1998, this latest Adaptation to 67/548/EEC contains major changes and additions. Many of the solvents used in CIJ inks are re-classified as to their hazards by the Adaptation (Table 4), forcing a re-classification of the ink. It is estimated that 80-90% of all i-CIJ inks will be affected. Member States have until 1st July 2000 to implement the changes.

Table 4. HS&E Data for Common i-CIJ Solvents

	MEK	EtOH	MeOH	Acetone	EtOAc
EU Class. 1999	F, Xi	F	F, T	F	F
EU Class. 2000	F, Xi	F	F, T	F, Xi	F, Xi
R phrases 1999	11	11	11	11	11
	36/37	-	23/25	-	-
R phrases 2000	11	11	11	11	11
	36-	-	23/24/25-	36-	36-
	66-67		39/23/24/25	66-67	66-67
N symbol required?	NO	NO	NO	NO	NO
OES (8 hr)	200	1000	200	750	400
OES (15 min)	300	-	250	1500	-
OK BCF/CEPE?	YES	YES	NO	YES	YES

OES = Occupational Exposure Standard in ppm (UK equivalent to US TLV, OSHA & ACGIH); BCF = British Coatings Federation; CEPE = European Confederation of National Coatings Associations

A major factor in this upheaval is the introduction of two new Risk Phrases: **R66** "Repeated exposure may cause skin dryness or cracking", and **R67** "Vapors may cause drowsiness and dizziness". These phrases have been in use in Scandinavia for some time and are now to be incorporated EU wide. Many volatile solvents have been assigned the Risk Phrases, along with R36, R37, or R38, which also trigger use of the Xi irritant symbol. Common solvents, which will all carry Xi, R36, R66 and R67 are acetone, methyl acetate, ethyl acetate, n-propyl and isopropyl acetate, and MEK (which already carried the Xi symbol). Propan-1-ol and propan-2-ol will also carry the Xi symbol and R67.

The 25th Adaptation now classifies many solvents as 'Dangerous for the Environment' based on their aquatic toxicity. Indication of hazard is given by the use of a "dead fish dead tree" pictogram indicating danger to the environment (N) along with specified Risk Phrases. This includes most aliphatic hydrocarbons and some aromatic hydrocarbons (e.g. cumene). Ketones, esters and alcohols do not attract these hazards (Table 4). Presently, such classifications are used only in the EU, although their wider use via the Organization for Economic Co-operation and Development (OECD) may be a future development.

Future Adaptations to the Dangerous Substances Directive

A consultation document on the 26th Adaptation is expected to be available in the UK in early 2000. This will be a minor Adaptation. The chemicals listed in Annex 1 of the Dangerous Substances Directive are continually under review, and the current list of substances under review by the EU Working Group rather interestingly includes ethanol. The classification under review for ethanol is 'Toxic for reproduction Category 1: R61; Mutagenic Category 3: R40; Xn 48/20', although this was "agreed very low priority for discussion".

Dangerous Preparations Directive (88/379/EEC)

This covers the classification, packaging and labeling of ***mixtures of substances***, of which printing inks are a prime example. The same physicochemical and toxicological hazard categories are used as in the Substances Directive, and the H&S classification of the preparation is obtained via somewhat complex calculations based on the classifications of the individual ingredients and the amounts used. Software packages are available which automate the process (except flammability, which must be determined experimentally). Specific chemicals may have their own trigger concentrations, while (most) others use default concentrations defined by the Directive. Again, this information must be put on the container label and accompanying SDS.

New Dangerous Preparations Directive (99/45/EC)

This latest Directive (earmarked as 99/45/EC for intended release in September 1999) completely updates 88/379/EEC and introduces a requirement for the environmental classification of preparations, which offers the unappetizing prospect of the N symbol being displayed on the label of a CIJ printing ink. Default concentration limits of individual chemicals that trigger categorization of the preparation are shown in Table 5. The 'Dangerous to the Environment' category applies to the toxicity of chemicals to aquatic life; for i-CIJ inks the hazards are not normally solvents but rather the non-volatile constituents of the ink, such as biocide or colorant.

Table 5. Concentration Limit Criteria for Preparations

Substance Classification	Preparation Classification* (amounts in %)					
	N	N	N	-	-	-
	R50	R50-53	R51-53	R52-53	R52	R53
N, R50	≥25	-	-	-	-	-
N, R50-53	-	≥25	≥2.5<25	≥0.25<2.5	-	-
N, R51-53	-	-	≥25	≥2.5<25	-	-
R52-53	-	-	-	≥25	-	-
R52	-	-	-	-	≥25	-
R53	-	-	-	-	-	≥25

*(unless limits for a given chemical are specified in the Directive)

N = 'Dangerous for the Environment' symbol; R50 = Very toxic to aquatic organisms; R51 = Toxic to aquatic organisms; R52 = Harmful to aquatic organisms; R53 = May cause long-term adverse effects in the aquatic environment

As an example, we can take the case of the most widely used dye in i-CIJ, C. I. Solvent Black 29 (a chromium III / azo complex dye). One supplier classifies the dye as follows: N; R51-53. Using Table 5, we can see that if the ink typically contains 5% dye, this will trigger the R52-53 phrase but not the N symbol. In another example, C. I. Solvent Blue 136, the dye is classified as N; R50-53. If the ink again contains 5% dye, this triggers the N symbol along with R51-53. Dyes for water based CIJ inks may also carry environmental hazard warnings, making it somewhat difficult to claim the ink as environmentally friendly!

For these assessments, we are completely reliant on the suppliers of the colorant to carry out the appropriate tests and correctly classify their products. This leads inevitably to confusion since not all suppliers have done this. For instance, a non-EU supplier of C. I. Solvent Black 29 states no environmental hazards.

In addition to aqueous toxicity, the ‘Dangerous to the Environment’ category also applies to ozone depleting chemicals. i-CIJ inks do not contain CFCs or other ozone depleting chemicals. Dangerous Preparations Directive 99/45/EC will require implementation by Member States within 3 years of publication (i.e. by September 2002).

Other EU Directives

Solvent Emissions Directive (99/13/EC) was adopted in March 1999, with the aim of lowering ground level ozone production, and is intended to yield a 67% reduction in VOC emissions from specified solvent using industries by 2008. Member States have two years (until April 2001) to transpose the legislation into their national legal systems. The Directive defines a VOC as “any organic compound having at 20°C a vapor pressure of 0.01kPa or more”. Manufacturers of CIJ inks (>100 tonnes/year) will need to meet the specified emission limits from their factories. Users of CIJ printers will fall below the consumption threshold of the Directive and will be exempted.

Biocides Directive (98/8/EC) needs implementing in Member States by May 2000. Ultimately only those biocidal products which contain an active substance that is listed in Annex 1 will be authorized for use.

Safety Data Sheets Directive (91/155/EEC, amended by 93/111/EC) requires that safety data sheets be produced and supplied to the user for all substances and preparations defined as dangerous. Information must be supplied in a standardized 16-section format. The SDS pulls together data from all the areas discussed above.

Future Trends

The EU continues to lay down a raft of legislation affecting the printing ink industry, leading to increasing pressure to innovate and reformulate. The challenge for the chemist is to marry the end user requirements with the constraints of the ink jet process, whilst complying with all relevant legislation.

In general terms, world solvent demand is expected to decline slightly[4] as users and suppliers increase their recycling capability. Within this trend, however, the proportion of CFCs and hydrocarbons will reduce whilst the proportion of oxygenated solvents (alcohols, ketones, esters, etc.) will grow[4] due to their relatively favorable HS&E profile. These are exactly the types of solvents already in use for i-CIJ, so the expectation is that these types will continue to be used. The proportions of individual solvents may change, however. One can anticipate a continuing gradual increase in the use of ethanol, both on its own and in blends with other solvents (e.g. acetone, ethyl acetate) in an effort to match the excellent properties of MEK based inks. Alternative ketones may gain some market share. Methanol is expected to decline in use. Water will also increase in use where application requirements allow.

These changes will not take place overnight. There is an in-built inertia to change - namely, the existing field population of printers using (mainly) MEK based inks. Rather, there will be a gradual change and no one solvent will dominate as MEK has in the past. The demise of MEK has long been predicted; the fact that MEK is still and will continue to be a major solvent in i-CIJ is testament to its excellent technical properties. Like most widely used solvents it has come under increasing HS&E scrutiny and there will continue to be regulatory pressure on its use, but this applies to almost every solvent. There is no one perfect solvent; the fall out from the phasing out of CFCs and resulting efforts to devise replacements may lead to the emergence of a new “ideal” solvent, but this is currently a hope rather than an expectation. Thus any chosen solvent has properties which are a trade-off of good versus bad.

The innovative chemist has other options in addition to solvent choice. Careful choice of raw materials will enable higher solids inks to be developed, although this is a tough challenge giving the viscosity restrictions placed on the i-CIJ process. Increased use of water will reduce VOC emissions but this must be balanced against diminished ink performance. Polymer manufacturers are beginning to notice the CIJ sector as volumes (and potential revenues) rise, and are developing products which may allow great strides to be made in water based inks. Possible use of curable inks may allow solventless systems to be developed; however, these often have their own HS&E issues.

The end user will need to question his main priorities. By accepting a longer drying time, engineering more time in his process for the ink to dry, or providing a drying stage on his line, alternative systems including water may become viable. If the end user is more flexible in his requirements, this is always appreciated by the chemist!

Any developer of ink jet inks, whether industrial or consumer, solvent or aqueous, who intends to supply to the EU, needs to develop with these regulations in mind if his company wishes to be seen as environmentally responsible. It is up to suppliers of CIJ inks to offer alternatives and let market choose its direction.

Acknowledgements

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References

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Biography

Richard Marsden received his degree and Ph.D. in Colour Chemistry from the University of Leeds, followed by postdoctoral fellowships in synthetic organic chemistry at McMaster and Hull Universities. He moved into the ink jet field with Elmjet where he worked on CIJ inks for binary systems, before joining Linx Printing Technologies in 1990. As the Ink Development Consultant at Linx, he has a brief to investigate and develop IJ ink technologies for the future. He is a member of the Royal Society of Chemistry.