Cool Flash

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ENGENIOUS COOLANTS

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EDITORIAL

Environment is often a big concern in projects involving the use of a heat transfer fluid. In this sense, a thorough understanding of what biodegradability means, and the difference with toxicity, is important. Both properties are essential in the entire REACh registration program. And despite the general less positive economical climate, the entire chemical industry has and is still spending huge amount of efforts and resources to comply with these new directives. And there is even another change in legislation coming up : GHS. All of these haven been covered in this Coolflash. Enjoy reading. And enjoy the upcoming holidays!

IN THIS EDITION :

BIODEGRADABILITY

By Steven Poppe

The definition "Biodegradability" is often confused with "Toxicity". A substance, component, or product is called **biodegradable** if it can be converted by living organisms into its basic components, (for example into carbon dioxide and water). **Toxicity** means the degree to which a substance, component, or product is able to damage an exposed organism. A biodegradable substance could be converted by living organisms, but that does not automatically mean that the product is non-toxic. Moreover, a biodegradable substance could be decomposed into toxic components, depending on the chemistry of the substance.

If we are talking about Biodegradability, we assume that all, or a big part of a substance is relatively fast decomposed. What is meant with "a big part? And what does "relatively fast" signify? In the EU a substance is considered to be "Readily Biodegradable" if more than 70% of the substance is converted within 28 days. The definition supported in the EU regulation is "the extent to which degradation into carbon dioxide (CO_2), water and minerals takes place".

The choice of a suitable or relevant method to determine biodegradability is mainly based on the physical characteristics of the substance, such as: solubility in water, volatility, adsorbing capacity and so on. These characteristics determine which parameter would be suitable to monitor the biodegradability process, such as:

- Decrease of dissolved organic carbon
- CO_2 formation
- O_2 (oxygen) consumption

More specifically, when studying the biodegradation process of Zitrec Heat Transfer Fluids, we have to consider the different Zitrec formulations separately. The base fluid used in the Zitrec products is different from product to product.

From Arteco to Zitrec

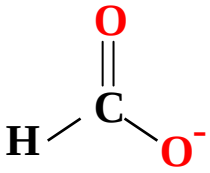
pH is a measurement expressing the acidity of the liquid. Our heat transfer fluids are slightly alkaline. Monitoring the pH of the liquid in the installation is a first quick check to evaluate the state of the fluid. Significant decrease indicate contamination and further analysis should to be done to define correct actions.

Zitrec Heat transfer fluids

BIODEGRADABILITY (cont'd)

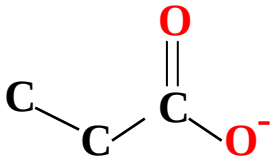
The following structures represent the different base fluids applied in the Zitrec fluids:

formate:

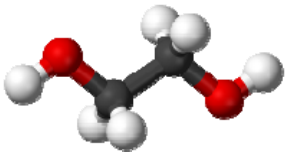


Legend:
H= hydrogen
O= oxygen
C=carbon

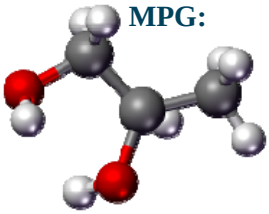
propionate:



MEG:



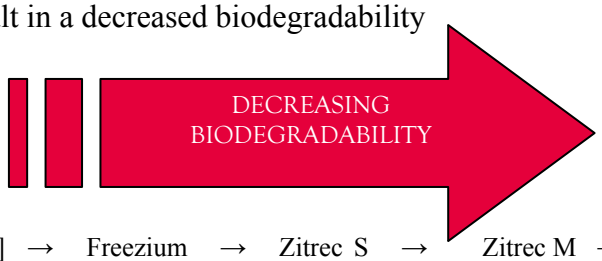
MPG:



Legend:
light grey/white= hydrogen
red= oxygen
dark grey/black= carbon

To convert these base fluid molecules into carbon dioxide and water, a certain amount of oxygen is needed. The more oxygen is needed, the more difficult the biodegradability process will take place at identical conditions. Secondly, the lower the oxidation level (number of oxygen atoms) of the base fluid molecule, the more difficult the biodegradability process will take place.

Also, with increasing carbon (C) in the molecule, also called increasing C-load, decreasing oxidation level result in a decreased biodegradability



[Zitrec A] → Freezium → Zitrec S → Zitrec M → Zitrec F & L

Beside the base fluid, there are also the Zitrec anti-corrosion additives to take into account for in the biodegradability equation. Both mineral (traditional) inhibitors as carboxylate inhibitors do not have a significant contribution to the carbon load in the formula and do not contain chemicals which are typically associated with difficult biodegradation.

So based on the above described theory, all the Zitrec Heat Transfer Fluids are readily biodegradable. Salt based Zitrec formulations are performing slightly better in terms of biodegradability, compared to the glycol based Zitrec fluids. (More info on biodegradability can be found on the product specific MSDS.)

Despite all the existing facts and theories on biodegradability, the real biodegradation process will take place at the moment at which the products are exposed to the environment. Depending on the prevailing environmental conditions (pH, temperature, concentration, micro-organisms,…), the biodegradability process could start. The start, the speed and completion of the Biodegradability of Zitrec, thus depends on these environmental conditions.

REACh – registration is ongoing

REACh - Registration , Evaluation and Authorization of Chemicals… the entire chemical industry has been immersed in this new regulation already for quite some time now, in order to pre-register the required substances. And yet, the work is only at an initial stage.

At this moment, chemical companies are preparing for **registration**. The first deadline of December 2010 for the first volume band is really not so far off anymore. Yet, this process for registration is still struggling a lot. This despite that, in order to facilitate the registration of 1 substance by a multiple number of companies, the concept of SIEF - Substance Information Exchange Forum - was set up. But although we are already more than 5 months past the pre-registration, this is still in many cases not fully or even hardly operational.

SIEF process

Members of a SIEF are the lead registrant, the SIEF facilitator, and the other registrants. Together they need to make up the full registration dossier, containing relevant tox date, safety & health information, a chemical safety report…. of the substance concerned. This 'joint' dossier must be submitted by the lead registrant first, before other registrants can make their registration. And although the closure date for the first volume band is 30/11/2010, it is obvious that the lead registrant must do this a few months in advance to allow other registrants sufficient time to complete their registration. CEFIC (= European Chemical Industry Council) recommends the lead registrant to submit this joint dossier by 01/05/2010. Here again, this will be a tight deadline to meet. But there's more to come!

Even though REACh implementation is still fully running, another change in chemicals regulation has came into force : **Globally Harmonized System.**

Globally Harmonized System

The Globally Harmonized System, also referred to as GHS, covers labeling requirements as well as requirements for the Material Safety Data Sheet. GHS was initiated already in the '80, and the need was really there to come to a globally uniform system of classification and labeling of chemicals. To illustrate this, Table 1 gives you an example of a dangerous substances and its classification according to the different regional regulations.

substance LD50 = 257mg/kg	
EU	Harmful
US	Toxic
Canada	Toxic
Austrialia	Harmful
Japan	Toxic
Malaysia	Harmful
New Zealand	Hazardous
China	Not dangerous
Korea	Toxic
GHS	Danger

Table 1

** LD50 : lethal dose for 50% of the population*

What is now the link with REACh?

In fact, REACh is not covering CRITERIA for classification & labeling. For this, REACh is still referring to the existing regulations which are :

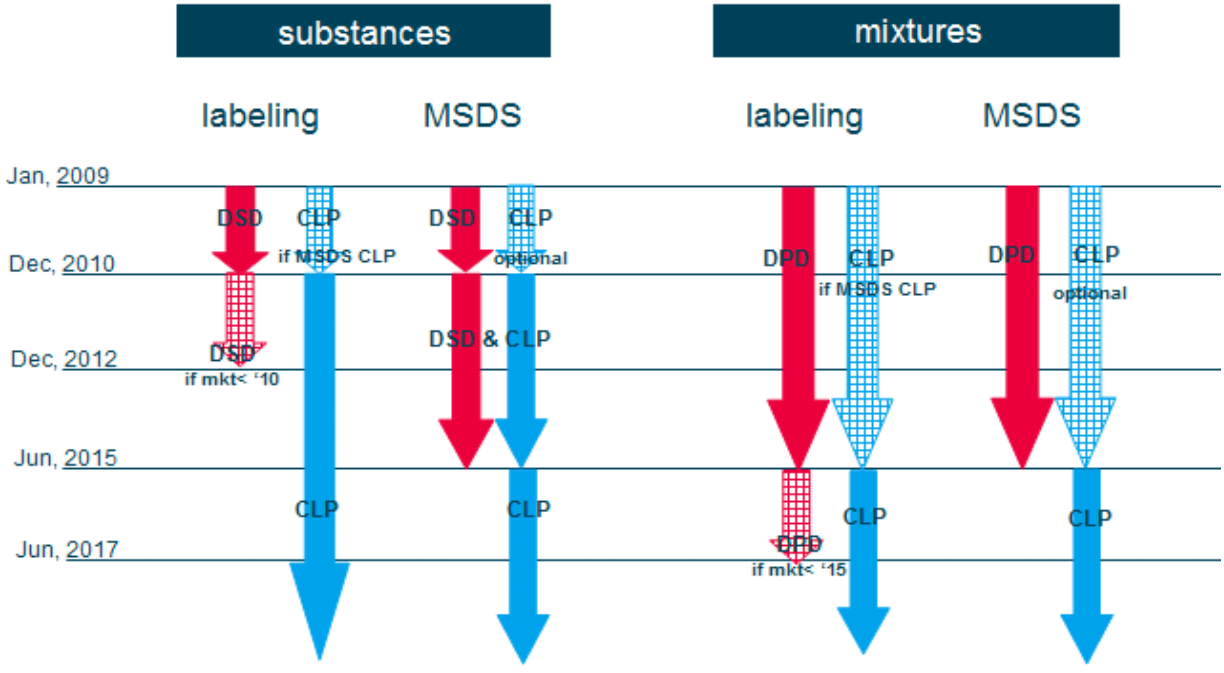
- Dangerous Substance Directive (67/548/EC) (also referred to as DSD)
- Dangerous Preparations Directive (1999/45/EC) (also referred to as DPD)
- Regulation on Safety Data Sheets (91/155/EC)

The new GHS will have different criteria and different cut off limits for classification, as well as a different approach on classification of mixtures, most probably leading to more severely classified mixtures, and as such increase the number of classified mixtures.

Implementation of GHS

GHS is a global approach, nevertheless the implementation will be region-specific. In Europe, this has resulted in the new directive Global Harmonization of Classification & Labeling of Chemicals (referred to as CLP regulation), directive EG 1272/2008. It came into force Jan 20, 2009, and from now will gradually replace the existing directives DSD and DPD. Table 2 shows the gradual implementation of this new directive for both substances and preparations.

Table 2



Impact of GHS

For sure, the impact of the new CLP directive will be a lot more visible to consumers. Besides the difference in criteria, an important difference of CLP versus the current regulation is the change on the label:

– A chemical labeled according to the GHS will look completely different versus what we know today. We are very familiar with the orange squares, containing the symbol of hazard. Not only will now the form of the **symbol** change, also some of the symbols itself are different. Table 3 gives you an overview of all GHS symbols.

Table 3

GHS01	GHS02	GHS03
• Explosives • Self-reactives • Organic peroxides 	• Flammables • Self-reactives • Pyrophorics • Self-heating • Emits flammable gas 	• Oxidizers • Organic peroxides 
GHS04	**GHS05**	**GHS06**
• Gases under pressure 	• Corrosive to metals • Skin corrosion • Eye Corrosion 	• Acute toxicity 
GHS07	**GHS08**	**GHS09**
• Acute toxicity • Skin irritation • Eye irritation • Skin sensitizers • STOT-Single 3 	• Respiratory sensitizers • Germ cell mutagens • Carcinogens • Reproductive toxicity • Target organ toxicity,1-2 • Aspiration Hazard 	• Aquatic toxicity 

– Additional to the classification, a **signal word** will be added on the label, indicating the relative level of severity of hazard, to alert the reader. This will be either 'danger', either 'warning'.

– And last but not least, further changes to the label are the replacement of Risk and Safety phrases, by **Hazard**-statements, and **Precautionary** statement, in some cases accompanied by a precautionary pictograms.

These shifts in regulation in the chemical industry are not only changing the landscape, but are also demanding time, resources and money! Registration is not for free, and investment will need to be made to allow systems to comply with new criteria for labeling and safety data sheets.

This "extreme make-over' will take still a number of years until final completion.

READ IN THE PRESS

Where it is always winter

This article is actually an extract from Panorama from 1935! It describes the production of a icerink in Amsterdam, based on a primary circuit on ammonia, combined with a secondary heat transfer fluid (brine). It is a nice exemple to demonstrate this is not a new process, although it must be said that it has been optimised since, a.o. the corrosion protection of secondary HTF have significantly improved.

Source RCC Koude & Luchtbehandeling , Dec 2008

Field frozen? Game on!

This article covers the production of a frozen baseball field for the NHL Winter Classic of hockey, via a huge mobile rink refrigeration unit. Also here this is done via ammonia in the primary circuit, but with a glycol-based HTF in the second circuit.

Source ACR News , Feb 2009

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Zitrec Heat transfer fluids