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The Impact of Reach and CLP Regulations on the Safety Management of Hazardous Materials Storage

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The new European regulations about management of hazardous substances and mixtures, including REACH and CLP Regulations, have introduced numerous restrictions on the use of certain chemical products. These restrictions have led to a reduction of some chemical commercialisation at the expense of others those not requiring special precautions to be used. However, the use of chemicals, although apparently not dangerous, requires careful management to prevent accidental contact between substances and/or mixtures that are incompatible each other.
In this paper it is presented a methodology to assess the compatibility of chemicals in a storage field of flammable and/or toxic chemicals, to be used in case a new chemical has to be introduced in the plant.
The method is illustrated through its application to a case study consisting in a storage field (Seveso site), storing about 70 chemical, where a modification has to be introduced in the use of a storage tank of dimethylcarbonate. In this case, the new chemical introduced is not dangerous from the Seveso Directive point of view but it is not compatible with halogenated hydrocarbons already stored in the storage field and dangerous for workers health. Therefore, the company has adopted a procedure to prevent the accidental contact between these chemicals during the operation of loading, stored and transport on the road.
It's important to notice that this approach allowed both to verify the compliance with Seveso regulations about modifications management and to identify the prevention measures to avoid accidental contact between chemicals, even if the chemicals apparently are not hazardous. The results obtained have been extended to management of all chemicals of the warehouse.

1. Methodological approach

The paper presents a methodology for the assessment of the compatibility between chemical agents: the proposed approach is composed by 4 steps, resumed by the Figure 1 in the following page.
The first step consists in the identification of chemical, physical, toxicological and ecotoxicological properties of the new chemical products, as described in their Material Safety Data Sheet (MSDS).
Then, it must be taken into account the compatibility between the new chemical products and the air, and/or the water, and/or the other stored chemicals, as well as the scenarios arising from an accidental contact of them, in accordance to the U.S. Environmental Protection Agency (EPA) document, "A Method for Determining the Compatibility of Hazardous Wastes" (Hatayama et al., 1980) (Step 2)
The information about accident scenarios derived from the application of compatibility matrix (Step 2) is later integrated with the results of the historical analysis accidents in chemicals storages (Step 3).
The final step is the development of a risk analysis, in order to verify that the modification introduced doesn't entail an increase in the existing risk level, in accordance with the Seveso laws and the Regulations for Safety and Health in workplaces (Step 4).
The proposed approach was applied to a Seveso storage plant, and its development is explained in the next paragraphs.

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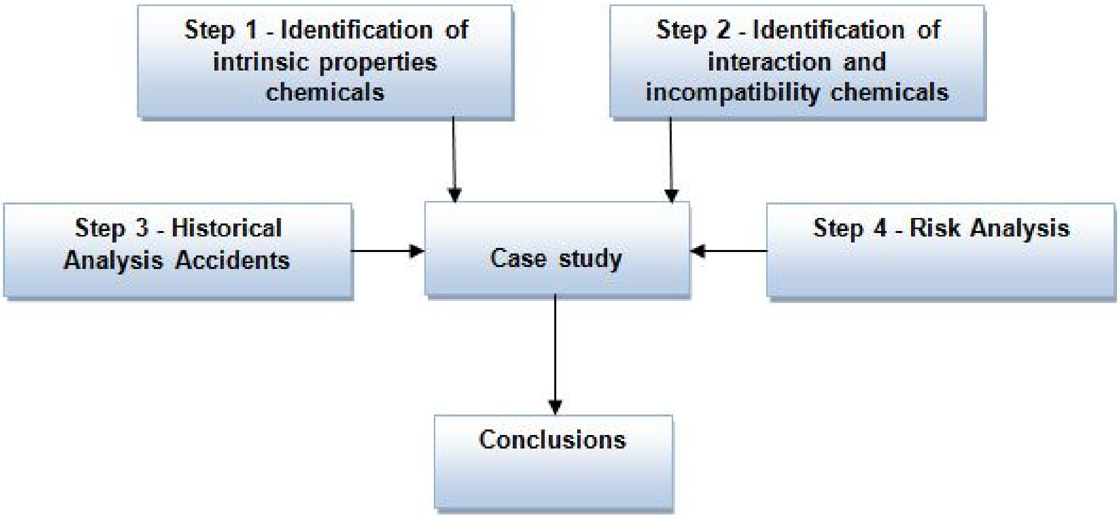

Figure 1: Scheme of the proposed approach

2. Step 1 - Identification of the intrinsic chemical properties

The identification of the intrinsic chemical properties of a substance or a compound - chemical, physical, toxicological and ecotoxicological characteristics – is provided by its Material Safety Data Sheet (MSDS); in order to use this document in the analysis, it has to be updated, compliant with REACH Regulation and complete of Exposure scenarios.
In our case study, we especially analyzed the MSDSs of two chemical agents, the Dimethyl carbonate and the dimethylformamide; indeed, the plant management wanted to replace for commercial needs the first agent with the second one. With reference to the European Directive 67/548/CE and the CLP Regulation, the first agent is classified with the Risk phrase R11 and the Hazard identification H225, and it is subjected to the regulations of the Italian Seveso law (Legislative Decree no. 334/1999); the second one is classified R20/21, R36, R61 and H360D, H332, H312, H319, and is not subjected to the Italian Seveso law. Therefore, the replacement of the Dimethyl carbonate with the dimethylformamide had the advantage of a reduction of the quantity of flammable substances stored; but the analysis of the MSDS of dimethylformamide showed a problem of incompatibility with other chemical agents stored in the plant, especially with the halogenated hydrocarbons (see Figure 2 below)..

Section 10 - Stability and Reactivity

Chemical Stability: Stable at room temperature in closed containers under normal storage and handling conditions.
Conditions to Avoid: Mechanical shock, incompatible materials, ignition sources, excess heat, temperatures above 55°C.
Incompatibilities with Other Materials: Carbontetrachloride, violent reaction with halogens, iron, oxidizing materials, chlorinated hydrocarbons, isocyanates, nitrates, organic materials, phenols, ammonia, anhydrides.
Hazardous Decomposition Products: Carbon monoxide, oxides of nitrogen, irritating and toxic fumes and gases, carbon dioxide.
Hazardous Polymerization: Will not occur.

Figure 2: Extract of the Section 10 of the MSDS of Dimethylformamide

Consequently, the Service for the Prevention and Protection of the plant asked us an assistance in order to evaluate how to manage this incompatibility, and how to verify the other possible incompatibilities between the chemical agents already stored.

3. Step 2 - Compatibility analysis criteria

After the consultation of the MSDS of the analysed products (step 1), it was necessary to evaluate the incompatibilities between the chemical agents. In order to evaluate the possible interactions, first of all it is necessary to remind the most recurring cases of incompatibility:

1) Chemical agents which violently react in contact with water: they generate flammable and/or toxic gas, or activate violent reactions. The chlorinated substances belong to this category: indeed they violently decay in contact with water, producing heat and toxic gas such as the hydrochloric acid.

2) Toxic chemical agents produced by conflicting chemical substances: the mixture of the substances could produce toxic gas releases, such as the hydrogen cyanide, derived from a reaction between acids and cyanide.

3) Conflicting chemical agents at risk of violent reactions: they can violently react, provoking sometimes an explosion. The hydrocarbons could assume this behaviour in contact with chromic acid, bromine, chlorine, fluorine and peroxides.

4) Oxidant chemical agents: they aren't spontaneously flammable, thus they represent a source of oxygen which can facilitate the combustion and immediately react in contact with reducing agents. The liquid oxygen and some concentrated acids (nitric acid, sulphuric acid, perchloric acid, chromic acid) belong to this category.

5) Explosive chemical agents and union of potential explosive reagents: if subjected to impact, friction, heat, light or catalytic contaminant, they could auto-react and decay producing violent explosions. The acetylene mixtures and the deriving salts, the mixtures containing nitrogen, the peroxides and the vinyl compounds belong to this category.

The EPA document previously mentioned (Hatayama et al., 1980) provides a methodology for a quick assessment of the incompatibilities: it proposes a categorization based on the chemical basic characteristics of the chemical agents (i.e. aldheydes, ketones, esters), identifying 41 different chemical groups. Then, the Figure 6 of the EPA provides a matrix to identify the incompatibilities between each chemical group, indicating also the expected scenarios deriving from the contact (i.e. H = heat generation, F =fire, GT =toxic gas formation, E = explosion). The matrix, shows in the Figure 3 below, allows to quickly identify the conflicting chemical agents, and to evaluate the consequences of their interaction; after this, it is easier to find and adopt the best technical, organizational and procedural measures to avoid the contact between the agents.

Reactivity Group No.	Reactivity Group Name										
1	Acids, Mineral, Non-Oxidizing	1									
2	Acids, Mineral, Oxidizing		2								
3	Acids, Organic		G, H	3							
4	Alcohols and Glycols	H	H, F	H, P	4						
5	Aldehydes	H, P	H, F	H, P		5					
6	Amides	H	H, GT				6				
7	Amines, Aliphatic and Aromatic	H	H, GT	H		H		7			
8	Azo Compounds, Diazo Compounds and Hydrazines	H, G	H, GT	H, G	H, G	H			8		
9	Carbamates	H, G	H, GT						G, H	9	
10	Caustics	H	H	H		H				H, G	10

Figure 3: Extract of the incompatibility matrix (Hatayama et al., 1980)

In our case study, we defined a reference excel database based on the principles of the incompatibility matrix, that we used to assess the chemical compatibility of the entire list of chemicals stored in the plant. The Table 1 shows in the column 3 the list of chemical agents stored; the column 1 and 2 identify the code and name of the chemical group to which each substance or compound belongs to. Column 4 shows the interactions with the other chemical groups, indicating the code.

Table 1: Chemicals product groups stored.

Hatayama matrix code	Group	List of chemicals products	Interaction with other groups
4	Alcohol glycol	Butyl alcohol, ethyil alcohol 94° and 99.9°, isopropyl alcohol, isobutyil alcohol, methyl alcohol, n-butyl alcohol, propylene ethyl glycol	1, 2, 3, 8, 18, 21, 25, 30, 34, 104, 105
6	Amides	N,N - Dimethylformamide (DMF).	1, 2, 21, 24, 104, 105
13	Esteres	Butyl acetate, Ethyl acetate, iso-butyil acetate, propylene methyl glycol acetate, butyl phthalate.	1, 2, 8, 21, 25, 102, 104
16	Aromatic hydrocarbons	Nitrous diluent (273,375,378,480), toluene, xylene, furnace oil solvent	2, 104, 105
17	Organic halogenates	Perchloroethylene, trichloroethylene	1, 2, 7, 8, 20, 21, 22, 23, 25, 30, 104, 105
19	Ketones	Acetone, acetone (high purity), methyl ethyl ketone, methyl isobutyl ketone	1, 2, 8, 20, 21, 25, 30, 104, 105
29	Saturated aliphatic hydrocarbons	Cyclohexane, dichloropropane, dichloromethane, heptane, hexane, gas oil, lampante petroleum.	1, 2, 5, 30, 104
28	Unsaturated aliphatic hydrocarbons	White spirit, unflavoured white-spirit, “3 stars”, Vegetable white-spirit	2, 104

The application of the Hatayama matrix demonstrated that there weren’t macro-incompatibilities between the chemicals originally stored in the plant. These results were confirmed also by the analysis of MSDSs. Thus, as far as concerns the dimethylformamide (amides), the adoption of the matrix wasn’t very meaningful: indeed it didn’t confirmed the incompatibilities of the product with halogenates hydrocarbons and halogens, indicated in Section 10 of MSDS.

4. Step 3 – Historical Analysis accidents

In order to integrate the results of step 2, we proceeded with an Historical Analysis: it permits to collect adequate data to formulate likely hypothesis concerning the relevant accidental events, through the examination of a series of records related to accidents happened in plant similar to the one analysed. The Historical Analysis evaluates the causes of happened accidents in order to identify the risk factors which could facilitate the accidental event: it highlights the critical operations, areas, or equipments of a certain typology of plants, and points out causes and consequences of the accidents.

In our case study, the research was conducted using the database MHIDAS (Major Hazard Incident Database Service), updated up to 2007 by the UKAEA Research Agency SRD (Safety and Reliability Directorate) on behalf of English Government HSE (Health and Safety Executive). The database contains more than 7000 accidents, collected worldwide; the collection and analysis of these data started around the Eighties. The research on MHIDAS showed that the accidents registered in last 30 years concerning the dimethylformamide consisted in only 1 event: a transporting accident, in which a tanker released dimethylformamide after an important impact. Therefore, the accident wasn’t related to the contact and reaction with Organic halogenates. No accidents were registered as far as it concerns operations of loading and unloading, drumming, and storage of the product.

The historical analysis involved also the Organic Halogenates and the Saturated aliphatic hydrocarbons stocked in the analysed plant: trichloroethylene, perchloroethylene, dichloropropane and dichloromethane. Any accident was registered for the first 2 agents; dichloropropane and dichloromethane were involved respectively in 1 accident and 14 accidents, but they weren’t related to dimethylformamide.

Finally, we also considered that the Historical analysis related to the analysed plant and the analysis of the operational experienced updated to 2009 never had highlighted anomalies and accidents in the unloading operations due to a mistake in the storage placement.

5. Step 4 – Risk analysis

A Seveso plant manager is bound to demonstrate for each modification operated in the plant, that it won't bring an increase in the risk level; for this reason he has to compile a Declaration of Non-Increase, and after this he can proceed with the foreseen intervention. In our case study, the change of intended use of the tank with the replacement of the Dimethyl carbonate seemed to be without any risk increase, according to the MSDS of the dimethylformamide. Indeed the new chemical agent was a non-Seveso one, and it brought a reduction in the quantity of the flammable substances stocked (see Step 1). Thus, since the identification of the chemical incompatibilities, it was necessary also to verify the possible existence of relevant accidental events. Therefore, we proceeded with the first step of the Risk analysis, identifying all the operations related to dimethylformamide and their specific hazards. Notice that, since the analysis concerned a new equipment, characterized by a great simplicity (it wasn't foreseen a process, but only the handling of the agent), we took into account even the technical, organizational and procedural measures that the Plan management minded to adopt. The operations and the preventions measures consisted of:

- <u>Pouring form the tanker to the tank</u>: in order to avoid an accidental contact of the product with halogenated compound, were foreseen dedicated devices for the handling of dimethylformamide (pumps, hoses). Furthermore, were reviewed the operative instructions related to the operations of loading and unloading, drumming, and storage of the product. Any operation with dimethylformamide was permitted only to informed and trained staff.
- <u>Replenishment of the tanker from the tank</u>: in order to avoid the loading of dimethylformamide in tanker partitions that previously had contained halogenated hydrocarbons, it was inserted a block code in the program for the formulation of the loading seals, used by the logistic office. The block code impedes the issue of the loading seal (which is compulsory for the transportation) if the tanker which has to be filled with dimethylformamide previously contained halogenated hydrocarbons or whether could be present some halogenated hydrocarbons in the partitions of the tanker. It was updated the operative instruction I/OP 910, in order to inform and train the staff about the new procedures to avoid the contact of incompatible compounds, and the same procedure was adopted for the handling of exiting drums, in order to avoid loading on the trucks drums with dimethylformamide together with drums with conflicting agents.
- <u>Moving from the tank to the drumming line</u>: before the drumming, it was foreseen the loading of the product on a tank, later connected to the drumming plant. The latter was destined to chemical agents compatible with dimethylformamide; anyway it was foreseen a pump exclusively dedicated to the product. The drumming operations were re-organized through the review of the operative instruction"I/OP 910/1 Drumming".
- <u>Storage in depository</u>: it was foreseen the storage in 200 l. drums, for a maximum quantity of 9 drums. The warehouse A was destined to dimethylformamide storage, while the warehouse B (the farest from the first one) was dedicated to halogenated hydrocarbons. The handling was committed to educated and trained staff.

The risk analysis highlighted that for the operations of loading and unloading, drumming, and storage of the product, it was extremely unlikely the contact of the dimethylformamide with halogenated hydrocarbons.
As far as it concerns the work wealth and safety applications, the plant management committed itself to the adoption of the requested measures to grant the safety of workers, minimizing the exposition and adopting the prevention devices.

6. Conclusions

In the chosen case study, the replacement - due to commercial necessities - of a flammable chemical agent with another belonging to a lower risk category didn't represent an increase in the risk level, so that the plant administrator wasn't subjected to any other prescriptive fulfillment. Thus, the hazard related to the potential incompatibility of the new agent towards the existing chemical agents requires anyway a careful assessment, in order to identify the preventive and protective technical, organizational and procedural measures which are necessaries to introduce the new substance. Our assessment, which followed the steps indicated in the Chapter n. 1, produced the following results:
1) Previous identification of the hazards towards men related to the storage and employment of the dimethylformamide, and consequent review of the documentation about the assessment of the chemical risks, before the adoption of the new agent;

2) Identification of the possible incompatibilities between the new agent and the existing ones, and consequent adoption of an adequate Plan for the Information, Education and Training of the staff related to a safe employment and management of the new agent;

3) Adoption and implementation of a new series of specific operations related to the new agent;

Furthermore, the analysis also produced other important evidences for the compulsory Declaration of Non-Increase: the foreseen modification didn't introduce new typologies or modalities of events related to the major risk; and the fire risk was reduced with the introduction of the new agent.

The experience showed that the analysis of the incompatibility between chemical agents forms a basic part of the Risk Analysis, especially for the management of the modification due to the introduction of new chemical agents. Indeed they could be a risk for the health and safety of the workers, even when they aren't classified as hazardous by Seveso and/or Safety and Health Regulations.

Thus, in case of specific risks, an approach based on the quick assessment of the incompatibility - such as the Hatayama matrix - couldn't be sufficient: this kind of analysis should always be integrated with a careful evaluation of the MSDSs and a risk analysis, which can better define the actual hazards. The modifications introduced by the REACH and CLP regulations made the MSDSs an increasingly valid support in the analysis of incompatibilities: indeed they definitely strengthen the exactitude of the analysis thanks to the introduction of a greater quantity of information about the incompatibilities and especially the scenarios of exposure, related to the employments of the chemical agents.

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