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Incompatibilities of chemicals

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Abstract

Chemical incompatibilities are potentially significant problems where hazardous chemicals are found. A number of chemical segregation systems have been developed which provide recommendations for the separation of incompatible chemicals. Three segregation systems were identified in this study: the UN Dangerous Goods system (which uses physical hazard as the main reason for segregation and has 14 categories), the US CHRIS system (which uses chemical reactivity and has 24 categories) and a third system which uses environmental risks (and has 25 categories). These systems were combined. Merging of each system was initially problematic, but became considerably easier once certain characteristics had been defined (such as flammability or water incompatibility). This gave a final merged incompatibility table containing 100 different segregation groups. This research study showed that it was possible to combine different segregation systems based on different criteria and that more comprehensive segregation systems can be developed. These can be of use in the decision-making process about where groups of chemicals may be used, and during the use of chemicals, where chemicals should not be combined. The use of more comprehensive segregation systems will also assist in developing proper measures for their control. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Chemicals can be hazardous by themselves [1–3], and can present extra hazards when mixed with other chemicals [4–7]. This property is normally denoted as chemical reactivity, and keeping such additional (and unwanted) hazards apart underlies much of the disciplines of chemistry, chemical engineering and chemical manufacturing [8–10].

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While the mixing or reacting of chemicals is part of these activities, there are times when reactivity is not a desired endpoint [11]. When a reaction between two chemicals releases energy in a quantity too great to be dissipated by the immediate environment of the reaction system, the reaction becomes uncontrolled [7]. Chemical reactions may also release things other than energy, such as gases or pollutants. The problem of incompatibilities of chemicals is well-recognised [2,5–8,10,12–14].

Recognition that some chemicals should not be stored together began in the last century, when the mining industry learned from bitter experience that explosives required special storage, both in terms of where they should be stored, and what they might be stored with. This led to the introduction of stringent controls through Mines or Explosives legislation.

Other categories of chemicals were also recognised as requiring specialised storage during the early part of the 21st century, including compressed gases, flammable materials, poisons, corrosives and oxidisers. With the discovery of the military and industrial uses of radiation in the 1930s and 1940s, radioactive materials were recognised as another group of materials needing their own storage requirements. In time, many of these requirements were incorporated into regulatory initiatives such as Hazardous Materials or Dangerous Goods legislation. These initiatives also recognised that the storage or transport of reactive chemicals may occur in such a way that unwanted reactions produced, which had the potential to be dangerous to health or the environment, must be controlled safely [6,10,15–17].

Therefore, segregation of incompatible chemicals to reduce the associated hazards and risks is not a completely new concept.

2. Systems for chemical incompatibilities

The development of a significant number of groups of materials requiring different storage and incompatibility needs is offset by the commercial requirements of limited space and uncertainty about the hazards of stored materials. Safe systems for hazardous chemicals storage should be possible using basic rules [6,18]. In the 1950s, under the umbrella of the United Nations Expert Committee for the Transport of Dangerous Goods, a series of recommendations was developed for the classification, labeling, packaging and segregation of dangerous goods. These recommendations, commonly known as the Orange Book, are published regularly [19]. In Australia, these recommendations are given legislative force through state-based legislation and a national dangerous goods code [20].

However, while the UN Dangerous Goods system attempts to be a complete system, its very comprehensiveness can lead to problems. In some cases, the distinction between different categories of dangerous goods was based on physical, rather than chemical properties (e.g., poisonous substances are covered by Class 2.3 Poisonous Gases and Class 6.1 Toxic Substances). In other cases, the classification is too broad to assist in developing safe policies for segregation of groups. For example, UN Dangerous Goods Class 8 covers corrosive substances, and includes both acids and alkalis. In many cases, these two groups are incompatible, and should not be stored together, a combination

theoretically permissible if they are classified in the same class. Therefore, other systems have been developed which have targeted other properties (e.g., more specific aspects of chemical reactivity or effects on environment). Most notably, environmental effects of chemicals are a particular concern [16,17,21].

One such system is the US Coast Guard CHRIS system [22]. This uses chemical reactivity as its main focus. If the CHRIS system is compared with the UN Dangerous Goods system, some discrepancies occur. Similar discrepancies are likely with other systems for the storage or mixing of hazardous chemicals, which can lead to confusion.

Another system, originally suggested for hazardous wastes and with a focus on environmental aspects, is the incompatibility table proposed by Hatayama et al. [23].

The main aim of this study is to compare different segregation systems for incompatible chemicals in an attempt to investigate if they can be merged into a comprehensive system. Such a system could:

- Investigate if the combination of different segregation systems based on different philosophies and logic is possible;
- Assist in the design and development of a more comprehensive and precise segregation system for hazardous chemicals;
- Encourage other research works to be carried out in the design of more precise segregation systems by (among other things) merging different segregation systems;
- Provide a safer workplace and environment; and
- Increase the chemical safety information regarding segregation of chemicals.

3. Methods and results

The methodology for this project was conceptually fairly simple:

1. Combine the incompatibility recommendations of the Dangerous Goods system [20] and the US Coast Guard CHRIS system [22] to form an ‘‘interim-merged incompatibility system’’; and
2. Combine the interim incompatibility system with the hazardous waste incompatibility system of Hatayama et al. [23] to form a final merged incompatibility system.

Initially, the incompatibility table of the UN Dangerous Goods system [20] was combined with that of the US Coast Guard CHRIS system [22]. The main reasons for choosing to combine these two systems were that: first, there is some degree of similarity between the two systems; and second, the exercise of combining them could be used to develop an appropriate methodology and gain insights into the process.

The UN Dangerous Goods system is an internationally recognised system of chemical classification, which comprises nine classes as well as some subclasses of dangerous goods. These categories cover, in broad terms, the main groups of reactive chemicals. Therefore, it was decided to use the dangerous goods classification as the template for the merged incompatibility system. In most of these classes, the main hazards that have been considered in this system are explosion and flammability which are physical hazards. Even in the other classes of this system, except Class 6 (Toxic and Infectious Substances), priority has been given to physical hazards, particularly flammability. The recommended segregation of dangerous goods by this system has been shown in Table 1.

Table 1

The recommended segregation of dangerous goods by the UN Dangerous Goods system

1	Class 1	1																
2	Class 2.1	N	2															
3	Class 2.2	N	Y	3														
4	Class 2.3	N	Y	Y	4													
5	Class 3	N	Y ^a	Y	N	5												
6	Class 4.1	N	N	Y	Y	Y	6											
7	Class 4.2	N	N	N	N	N	N	7										
8	Class 4.3	N	N	Y	Y	Y	Y	Y	8									
9	Class 5.1	N	N	Y	N	N	N	Y	Y	9								
10	Class 5.2	N	N	N	N	N	N	Y	Y	N	10							
11	Class 6	N	Y	Y	Y	Y ^d	Y	Y	Y	Y ^b	Y ^b	11						
12	Class 7	N	N	Y	Y	N	N	N	N	N	N	Y	12					
13	Class 8	N	Y	Y	Y	Y	Y	Y	Y	N	N	N	Y ^d	N	13			
14	Class 9	N	Y	Y	Y	Y	Y	Y	Y	Y ^c	Y ^c	Y	Y	Y	Y	14		

Notes:

Y Represents a safe combination.

N Represents an unsafe combination.

a Means N when both classes are in bulk.

b Means N when Class 6 substance is a fire risk substance.

c Means N when Class 9 substance is a fire risk substance.

d See also ADG Code.

In contrast, the CHRIS system focuses on the main chemical hazards arising from reaction between chemicals. The segregation of chemicals by this system is shown in Table 2.

It is obvious that neither of these systems can cover all safety aspects in dealing with every chemical. In fact, in practical situations, a combination of all kinds of hazards is possible, and the final outcome would be a product of the interaction between the different sorts of hazards.

Furthermore, while the classification of chemicals in the UN Dangerous Goods systems is primarily mainly based on physical hazards, in the CHRIS system, chemical properties have been considered as the basis of the classification; and in reality, different classes in this system are more correctly described as chemical categories.

In attempting to merge the UN Dangerous Goods and the CHRIS systems, it became apparent that the merged segregation system was not truly representative of either system. Categories from each system had to be modified or new categories had to be developed. A major reason for this was that in neither of these two systems did classes of chemicals possess the same physical and chemical properties. There are a number of cases where combination of certain chemicals is not allowed in the UN Dangerous Goods system, while they may be allowable in the CHRIS system; or the reverse. For example, the Dangerous Goods system regards Corrosives as one class, whereas the CHRIS system regards Organic Acids, Inorganic Acids and Caustics (all Corrosives) as incompatible with each other. Also, some chemicals in the CHRIS classification, such as aldehydes or esters, can be classified into more than one UN Dangerous Goods class on

Table 2
The recommended segregation of chemicals by the CHRIS system

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	
1 Inorganic Acids	x																								
2 Organic Acids	x	x																							
3 Caustics	x	x	x																						
4 Amines and Alkanolamines	x	x	x	x																					
5 Halogenated Compounds	x	x	x	x	x																				
6 Alcohols, Glycols, and Glycol Ethers	x	x	x	x	x	x																			
7 Aldehydes	x	x	x	x	x	x	x																		
8 Ketones	x	x	x	x	x	x	x	x																	
9 Saturated Hydrocarbons	x	x	x	x	x	x	x	x	x																
10 Aromatic Hydrocarbons	x	x	x	x	x	x	x	x	x	x															
11 Olefins	x	x	x	x	x	x	x	x	x	x	x														
12 Petroleum Oils	x	x	x	x	x	x	x	x	x	x	x	x													
13 Esters	x	x	x	x	x	x	x	x	x	x	x	x	x												
14 Monomers and Polymerisable Esters	x	x	x	x	x	x	x	x	x	x	x	x	x	x											
15 Phenols	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x										
16 Alkyene Oxides	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x									
17 Cyanohydrins	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x								
18 Nitriles	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x							
19 Ammonia	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x						
20 Halogens	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x					
21 Ethers	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x				
22 Phosphorus, Elemental	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x			
23 Sulphur, Molten	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x		
24 Acid Anhydrides	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x

Note:

* Represents an unsafe combination.

the basis of main risk. This created a problem in merging the two systems, in that the underlying philosophies of each system were different (e.g., physical hazards as opposed to chemical reactivity).

Another example of the differences in underlying philosophies was that for each combination, the UN Dangerous Goods system provides a Yes/No answer. Apart from some minor footnotes (see Table 1), there is no ambiguity in this system. However, the CHRIS system only provides information on compatibility where the two agents should not be mixed; and no information is provided on permissible combinations (see Table 2). Presumably, the reason for this is that definitive information on all possible combinations is lacking. However, this lack of advice could create a lack of confidence by a user of the CHRIS system.

In combining the two incompatibility systems in Tables 1 and 2, an “interim-merged table” was created (not shown here because of space limitations). In this table, 14 UN Dangerous Goods categories and the 24 CHRIS categories expanded to 53 categories when combined into the interim-merged system of incompatible chemicals. Each final category of chemicals has more common properties; and as a result, the proposed incompatibility of chemicals was more characteristic of the group it represents.

Preparation of the interim-merged table raised some problems of a non-specific nature. The first problem is that there are some hazardous chemicals belonging to some subclasses of the UN Dangerous Goods system which are not included in the CHRIS system. This problem was solved by specifying NOS (Not Otherwise Specified) categories to those classes or subclasses of the UN Dangerous Goods system.

The second problem was that there are some chemicals in the CHRIS which are not included in the classification of the UN Dangerous Goods system. Consequently, since the main categories of the interim-merged table were chosen based on the UN Dangerous Goods system classes, those chemicals are not included in this table, too. For example, there were many US Coast Guard categories (alcohols, ethers, halogenated solvents ketones and so on) that were all technically included in UN Dangerous Goods Class 3 Flammable Liquids. While the criteria for inclusion in DG Class 3 is fairly straightforward (a liquid with a flash point below 61°C), this presented problems for comparing materials such as ethers, many of which had flash points below 61°C, and others which had flash points above 61°C. This problem was solved by specification of another main class to this table as NDG, an abbreviation for Non-Dangerous Goods referring to the UN Dangerous Goods system. Therefore, Ethyl ether is a flammable liquid of Class 3, and Ethers of NDG are not. This allows incompatibility on the basis of chemical group and physical property to be distinguished. It is noteworthy that while NDG chemicals are listed in the merged table, this does not necessarily mean that these chemicals are not hazardous.

The next step was to merge a third incompatibility system into the initial merged system. As the UN Dangerous Goods system is primarily (but not exclusively) based on physical hazard, and the US Coast Guard CHRIS system is primarily based on chemical reactivity, integrating systems based on using similar philosophies will not fully explore the complexities of issues in developing a final merged system. The selection of the third incompatibility system should therefore be based on incompatibilities not necessarily based on physical or chemical hazards.

Table 3
Incompatibility table of Hatayama et al. [23]

	1	2	3	4	5	6	7	8	10	11	13	14	15	16	17	18	19	20	26	27	29	30	31	33	34	
1 Acids, Mineral, Nonoxidising																										
2 Acids, Mineral, Oxidising																										
3 Acids, Organic		G, H																								
4 Alcohols and Glycols		H	H, F	H, P																						
5 Aldehydes		H, P	H, F	H, P																						
6 Amides		H	H, OT																							
7 Amines, Aliphatic and Aromatic		H	H, OT	H																						
8 Azo and Diazo Compounds, and Hydrazines		H, G	H, OT	H, G	H, G	H																				
10 Caustics		H	H	H	H																					
11 Cyanides		GT, GF	GT, GF	GT, GF					G																	
13 Esters		H	H, F																							
14 Ethers		H	H, F																							
15 Fluorides, Inorganic		GT	GT	GT																						
16 Hydrocarbons, Inorganic		GT	GT	GT																						
17 Hydrocarbons, Aromatic		H, F																								
17 Halogenated Organics		H, OT	H, F, GT						H, OT	H, G	H, OF	H														
18 Isocyanates		H, G	H, F, GT	H, G	H, P				H, P	H, G	H, P, G	H, G														
19 Ketones		H	H, F																							
20 Mercaptans and Other Organic Sulphides		GT, GF	H, F, GT																							
26 Nitriles		H, OT, GF	H, F, GT	H																						
27 Nitro Compounds, Organic		H, F, GT	H, F																							
29 Hydrocarbons, Aliphatic, Saturated		H, F																								
30 Peroxides and Hydroperoxides, Organic		H, G	H, E	H, F	H, G				H, OT	H, F, E	H, E	GT														
31 Phenols and Cresols		H	H, F																							
33 Sulphides, Inorganic		GT, GF	H, F, GT	GT																						
34 Oxidising Agents, Strong		H, OT	H, GT	H, F	H, F	H, F	H, F	H, F	H, F	H, F	H, F	H, F	H, F	H, F	H, F	H, F	H, F	H, F	H, F	H, F	H, F	H, F	H, F	H, F	H, F	H, F

Notes:
H Represents heat generation.
F Represents fire.
G Represents innocuous and non-flammable gas generation.
GT Represents toxic gas generation.
GF Represents flammable gas generation.
E Represents explosion.
P Represents violent polymerization.
S Represents solubilization of toxic substances.
U Means may be hazardous but unknown.
 Example: H, F, GT
 Represents heat generation, fire, and toxic gas generation.

The incompatibility system proposed by Hatayama et al. [23] was developed for hazardous wastes. As such, the basis for incompatibility is based on environmental properties, as well as some of the physical and chemical issues already explored in merging the UN Dangerous Goods and CHRIS systems. This system is shown in Table 3. Since this system also includes information on the outcomes of combinations of different groups of chemicals, it can be used to improve the interim-merged incompatibility system.

A number of minor amendments were necessary, before merging the Hatayama system with the interim-merged table. For example, some organic peroxides were not listed in the UN Dangerous Goods list. Therefore, specification of a final class as Organic peroxides of NDG under the NDG Class is appropriate in such circumstances. As another example, Class 7 (Radioactives) had to be split into Pyrophorics of Class 7 and NOS of Class 7 (this is because of the combination of two major hazards — flammability and radioactivity — in one specific group of chemicals).

One further source of information was quite useful in developing appropriate categories for the final merged system. This was information from the Hazchem system which was designed and developed by the United Kingdom Fire Services [20]. It provides emergency action codes (Hazchem codes) to inform the first responders or emergency services of the necessary immediate response actions to minimise the involved hazards and risks, and the effects of chemical spillage or chemical emergencies. This action code consists of a numeral followed by one or more letters. These indicate the type of extinguisher to be used, plus information on clothing, breathing apparatus, possibility of violent reaction and need for containment. Within Australia, the Hazchem code is normally required to be shown on an Emergency Information Panel (EIP) to be shown on vehicles transporting dangerous goods, or a placard to be shown on stores containing dangerous goods.

Since water compatibility is extremely important to extinguish the fires involved with hazardous chemicals, the Hazchem code can be used for this purpose as a guide for water incompatibility. Other properties, such as solubility in water, density and toxicity, were also used.

The combination of the Hatayama with the initial merged system to form the final merged incompatibility system is shown in Table 4.

4. Discussion

Despite many of the difficulties in designing more comprehensive incompatibility systems, this study has shown that is possible to merge different incompatibility systems [20,22,23], even if they are based on different philosophies, to create more accurate and precise incompatibility systems. While the study represents a “state of the literature” review that may change as new information becomes available, Table 4 is as good a comprehensive incompatibility system that can be created out of three fundamentally different incompatibility systems.

Theoretically, the final merged system in Table 4 can be used to provide safer storage areas, safer transport of chemicals and safer workplaces. With more and more attention

by regulatory agencies on improving safety, the need for better management of chemicals in the workplaces [24] is also increasing.

Any incompatibility system for chemicals is designed to assist the professional and other personnel involved in chemical safety to make decisions about whether particular chemicals should be handled or stored together, or not. Regarding this, the final incompatibility system created in Table 4 is one means of assisting this process. As this particular incompatibility table provides Y (yes) or N (no) entries for each combination of chemicals, it seems of particular use. This is in contrast with the US CHRIS or Hatayama incompatibility tables which contain many cells without providing any information at all. Of course, the presence of empty entries in these tables may represent the uncertainty of not knowing what can happen if two chemicals are combined — perhaps an empty entry is more conservative than one that says “yes”. However, it also places a doubt in the user’s mind about the confidence they can have about the data.

Nevertheless, Table 4 could be a useful resource in the planning and decision-making process.

Some chemicals cannot be combined, by law. This suggests that other groups of incompatible chemicals can be handled and stored together safely. In some cases, it may be possible to use, store, or transport incompatible chemicals together safely, provided that relevant codes of practices, safe working procedures, and reference to incompatibility systems, such as that in Table 4, are complied with.

Due to the increasing numbers of chemicals in commercial use and the increase of knowledge about chemical hazards, this research study represents a “work in progress” which needs validation and extension. Examples of where further research effort might be needed include:

- checking to make sure that all the “yes” entries are truly safe;
- extending new categories in the table where necessary; and
- identifying more chemicals that might be added to existing groups.

The possibility of extending the “yes” entry to provide more information on the results of each combination (as included in the Hatayama system) should also be considered.

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