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COMMITTEE OF EXPERTS ON THE TRANSPORT OF DANGEROUS GOODS AND ON THE GLOBALLY HARMONIZED SYSTEM OF CLASSIFICATION AND LABELLING OF CHEMICALS

Sub-Committee of Experts on the Transport of Dangerous Goods
(Nineteenth session, 2-6 July 2001, agenda item 11(c)(i))

GLOBAL HARMONIZATION OF SYSTEMS OF CLASSIFICATION AND LABELLING OF CHEMICALS

Physical hazards

Criteria for flammable aerosols

Transmitted by the Consumer Specialty Products Association (CSPA)

1. It seems that during the course of negotiations to develop harmonized approaches to the flammability of aerosol products, the position of the United States of America, as supported by the CSPA, and the various positions of the European Union, as supported by the FEA, have been very far apart on most issues.

2. One could logically ask why the CSPA and the FEA, both comprised of experts in the field of aerosol technology, could see the same issue so differently. Are not aerosols basically the same products on both continents? Don’t all reasonable people want to protect and preserve life and property? Are there practical, easy to understand ways to grasp the seemingly myriad ways of looking at flammability of aerosols?

3. While attempting to support the positions of the United States of America on what CSPA consider to be the remaining issues relative to spray products, CSPA will also attempt to provide answers to some of these questions.

The various screens and tests

4. Currently, for spray products, the UN/ILO Working Group on classification criteria for physical hazards is looking at a total of five screens and tests by which to judge these products for both consumer safety and transport purposes: Flammable Content, Chemical Heat of Combustion (Ch Hc), Ignition Distance Test, and Enclosed Space Ignition Test with two endpoints (Time to Ignition and Deflagration Density). Were these truly independent parameters, more of the time spent discussing them would have been productive.

5. However, a source of frustration has been due to the fact that there are only two independent qualities of an aerosol product which determine its flammability: how intrinsically flammable are the contents and in what form are these contents made available to an ignition source.

6. CSPA contends that by defining the Chemical Heat of Combustion and the Ignition Distance of a spray product, one has fully defined both the consumer hazard and the transport hazard relative to other, non-aerosol, products in trade. To illustrate:

Flammable content

7. This screen was originally intended to give manufacturers the option to avoid expensive and dangerous testing. One calculates the percentage of ingredients in the can that have flash points below 93 °C. This is an attempt to get at the question of how intrinsically flammable are the contents but it serves no purpose to that end that is not already covered by Chemical Heat of Combustion. CSPA has given examples of highly flammable formulations that would be classified non flammable by this method and of low flammability formulations that would be classified extremely flammable. Since the Chemical Heat of Combustion method calculates the effective Heat of Combustion for the total formulation by the percentage of all ingredients, it is a much more effective way of getting to the same conclusion without the exceptions cited.

Deflagration density

8. This end point of the Enclosed Space Ignition Test is a method of determining the Lower Flammability Limit (LFL) or Lower Explosive Limit (LEL) of a mixture as sprayed into an enclosure. In essence, what we are measuring is how much fuel must you spray in order to get to the fuel/air ratio needed to support combustion.

9. While attempting to build a predictive model of Deflagration Densities for a range of formulations by calculating the effective LEL of the mixture based on molecular weight percentages, CSPA came across a memorandum to the FEA by Johann Visser of Akzo Nobel, the Netherlands, in which he hypothesized that the LEL of a mixture and therefore the deflagration density of a product can be simply defined by Heats of Combustion. CSPA agrees strongly with this hypothesis noting both the excellent agreement between its method using published LEL's and Visser's method using Heats of Combustion and the fact cited in his paper that several Universities had validated this concept empirically. Table I shows the range of commercially available products for which formulations were known and the prediction of LEL by both methods. Deflagration Density, calculated by the LEL method, is also shown.

10. Of the three parameters describing inherent flammability of the contents, CSPA believes Chemical Heat of Combustion is most robust. It takes into account Flammable content and predicts Deflagration Density.

11. One could argue that a test is more accurate than a theoretical prediction. From what little experience CSPA has had with Enclosed Space Ignition test, CSPA does not believe this to be true. At least 12 replicate tests on the same formulation with the same valve and dip tube and same operator would be necessary to determine a standard deviation for the test with 90% confidence. Ideally, this should be followed by additional replicate tests to determine multiple operator deviation. CSPA has not done this replicate testing, but believe, from the limited testing it has done, that the test itself may impart error in the range of ±25% for the more highly flammable products and perhaps even more for the less flammable products. CSPA believes much of this variability is due the fact that there is no fuel/air mixing in the test and, within the time frames of the testing, non-uniform clouds of gas at varying concentrations can travel within the enclosed space randomly. CSPA has also observed less volatile formulations running out of the drum onto the floor.

12. At this point, CSPA reiterates that it does not have much experience in enclosed space testing in the United States of America. The FEA has pointed out that the analogous 1952 "drum test" is still part of the United States Department of Transportation codes. However, for the past 25 years, an estimated 99.8% of all United States aerosols in commerce have operated under modern rules, which do not require the performance of this test.

Time to ignition

13. This test, like the Ignition Distance Test, attempts to get to the question of what form the flammable contents are in when they get to an ignition source. We all can imagine the difficulty in getting a large log of wood ignited by holding a match to it. Is the log flammable? If our definition of flammability is "can it be ignited by holding a match to it?" then, no. However, we all also know that if we reduce the log to sawdust, and throw this dust into the air and then light a match, we are likely to create an explosion.

14. We also know that liquids do not burn. What burns is the vapor hovering atop the liquid. The very concept of most spray aerosols is to deliver a fine mist of what are otherwise liquids as they sit in the can. By doing so we break up the liquid pool into fine particles, increasing the total available surface area and the amount of vapor available.

15. A significant part of the development of a commercial aerosol product is in selecting the combination of formulation, pressure, valve and dip tube. All these together will determine what we refer to as the "spray characteristic" of the final product. For some products, one will want an extremely fine spray. For others, a more coarse spray is desired. The desired amount of material delivered per second also varies according to the intended use.

16. The Time to Ignition parameter is a measure of how quickly the proper quantity (deflagration density or heat of combustion) of flammable material will get to the flame as a vapor. A fine spray of high Ch Hc material will deliver the small amount necessary for ignition much more quickly that a coarse spray wherein the flammables may be vaporizing slowly through a lot of water or low-volatility solvent. This is intuitive. It is also intuitive that the same properties that made that fine spray go quickly in this test will also cause it to ignite from a further distance in the Ignition Distance test. The same logic applies in reverse to the coarse, water bearing spray. In short this test appears to tell us nothing that the Chemical Heat of Combustion analysis and Ignition Distance test have not already told us.

CSPA positions

17. However, allowing for the potential for unique properties that may have not been fully considered, and in the spirit of harmonization, the CSPA has reluctantly supported discussion of all these tests and screens, both individually and in conjunction with each other.

18. At this point CSPA is committed to the principal that, **for the average range of aerosol products, the criteria and standards for the redundant screens and tests should result in consistent classifications and that no standard should be arbitrary and capricious**. For example, we do not believe that a product which, by ChHc and Ignition Distance would be non-flammable should be arbitrarily classified extremely flammable solely because of Flammable Content. Nor do we believe a product we know to have very high ChHc and would likely fail the Ignition Distance test should be classified non-flammable.

19. CSPA believes that the limits described in the report of the UN/ILO Working Group for Flammable Content are arbitrary and capricious if allowed to stand by themselves as some have interpreted. CSPA and FEA will be jointly proposing modifications to this that would preserve consistency.

20. CSPA has already agreed to a limit of 15 cm in the Ignition Distance test to define the break point between Flammable and Non-Flammable. This was a significant concession as current United States law sets the limit for an analogous test at a number which could be compared to 50-60 cm in the Ignition Distance test. This limit alone will result in the majority of aerosol products both in the United States and in Europe being classified at least Flammable. A significant number of United States products which are currently considered non-flammable will be caused to be re-classified by this agreement. Our goal is that the Flammable/ Non-Flammable criteria for the other tests would at least be consistent with this limit for "normal" aerosols.

21. However, it appears that the greatest disagreement between CSPA and FEA positions exists in the definition of limits to define the break point between Flammable and Extremely Flammable. Aside from the widely discussed differences between European Union adherence to the Precautionary Principle and United States reliance on Risk Management there are fundamental differences in aerosol products offered in commerce in the European Union and the United States. We believe the United States proposals for limits defining Extremely Flammable may serve the purposes of both entities because of these product related differences.

22. **Some notable differences between United States and European Union Products are**:

(a) Labelling- All US aerosol products, whether Flammable or Non Flammable, are required to prominently display a warning stating "Contents under pressure. Do not puncture or incinerate. Do not store at temperatures above 120 degr. F. Keep out of reach of children." We do not know of any similar requirement in the EU;

(b) Flammability Labelling- For the majority of aerosol categories in the US, Flammability warnings are required to be prominently displayed on the front panel of the can. All EU cans we were able to find had the warnings on the back panel;

(c) Personal Care Products- The European aerosol markets are much more heavily dominated by Personal Care aerosols. The seven year average through 1999 of reported aerosol fillings in the UK that were Personal Care products was 72%. The corresponding number for the US was about 32%. Aside from shave creams and hair mousses, Personal Care products are largely alcohol/ propellant based;

(d) VOC limiting regulations- Since 1989, the US formulators have been increasingly challenged to provide aerosols to meet environment-driven VOC limiting laws. To-date, no such limitations affect major commercial markets in Europe. The result of these US laws has been that the preponderance of US aerosols now contain water. For example, most hairsprays sold in 85% of the US contain 15% water. Most hairsprays in the rest of the country contain 40% water and this regulation will be, in effect, national in a few years. The vast majority of European hairsprays contain no water at all as it is, in general, deleterious to product performance. This results in a significant difference in the inherent flammability of the very large hairspray category between the continents;

(e) Consumer Preferences- It has long been said that even pre-VOC controlled hairsprays would be too wet for the European consumer. The average European hairspray contains nearly twice as much propellant relative to the alcohol and/or water than US brands do in order to attain the dryness of spray the European consumer prefers. This also adds to the inherent flammability of the contents.

23. The CSPA and the United States regulatory agencies responsible for consumer and transport safety regarding aerosols believe strongly that over-warning can sometimes be as hazardous as under- warning. We believe that a person warned of Extreme Flammability for a relatively innocuous product will develop behaviors and attitudes towards this label which will not serve him well when confronted with a product that has the same warning but is inherently more dangerous.

24. To this end, we have proposed limits for the Extremely Flammable classification which we believe will isolate those products that millions of dollars and decades of testing and experience have shown to present a significantly increased hazard over those we would consider Flammable.

25. The following Tables and Chart serve to illustrate the proposals relative to Deflagration Density and Time to Ignition.

26. Table II, part A, shows the results of testing performed in the United States on actual products in which the formulation was known. The products labeled “Euro” were European formulations sold by United States companies for their European distribution as no comparable US products were available in these Ch Hc ranges due to VOC restrictions. The deviation from predicted values is felt to be largely due to the inherent errors in the testing and we believe, in general, that there was good correlation.

27. Table II (b), part B, shows selected items from the previously submitted tests performed for the FEA wherein the general formulation could be readily discerned from the propellant and flammable contents data presented. Since only Time to Ignition was reported, the effect of the flow rate of the valve cannot be determined. We believe most aerosol sprays are designed to deliver product between about 0.5 g/s and 2g/s. Given this assumption, it is possible the EU data might also correlate well with the predicted values.

28. Given this predictive tool and a general knowledge of aerosol formulations as they are applied to categories of products along with published data that show the quantities, in cans produced, of the various product categories for different countries, one can roughly estimate the impact of various criteria for the countries.

29. For instance, we know from published data that, in the UK in 1999, 172 million cans of hairsprays were sold out of a total of 1262.6 M cans of all aerosols sold in the UK that year. We estimate that the average hairspray sold in the UK contains 4% resin, 30-50% hydrocarbon and/or DME propellant, and the balance ethanol. From these assumptions, one could calculate that at least 13.6% of all UK aerosols

had a Ch. Heat of Combustion of 27-30 kJ/g, and therefore a calculated Deflagration Density of approximately 70 or less.

30. By applying this same exercise to the other aerosol categories for both the UK and the US, and plotting Calculated Deflagration Density against the percentage of cans within specified ranges of DD for the two countries, one gets a graphic picture of the difference between the two markets. In the Chart we see that, while about 20% of products in both countries have DDs > 600g m^3, there is a marked difference in the rest of the chart. The FEA proposal for products exhibiting less than 150 g/ m^3 would result in 77% of UK aerosols and 69% of US aerosols being classified Extremely Flammable. This would leave about 3% of UK aerosols to be classified as Flammable.

31. The CSPA proposal of 70 g/ m^3 would result in 72% of UK aerosols, nearly all that would have been covered in the FEA proposal, being classified Extremely Flammable, while 31% of the US aerosols would be similarly classified. We believe the CSPA proposal satisfies the desires of both associations and reflects the formulation differences between the two continents.

32. CSPA also strongly believes that the types of products which have calculated DDs less than 70 g/ m^3 and Ch Hc greater than 30 kJ/g are distinctly more hazardous than the next lower level of flammable products. We have seen this distinction in fire testing with multiple pallets and in flame extension tests with individual cans. We believe both the consumer and the transport industry will be best served by having two classification levels only if there is a meaningful difference between these levels.

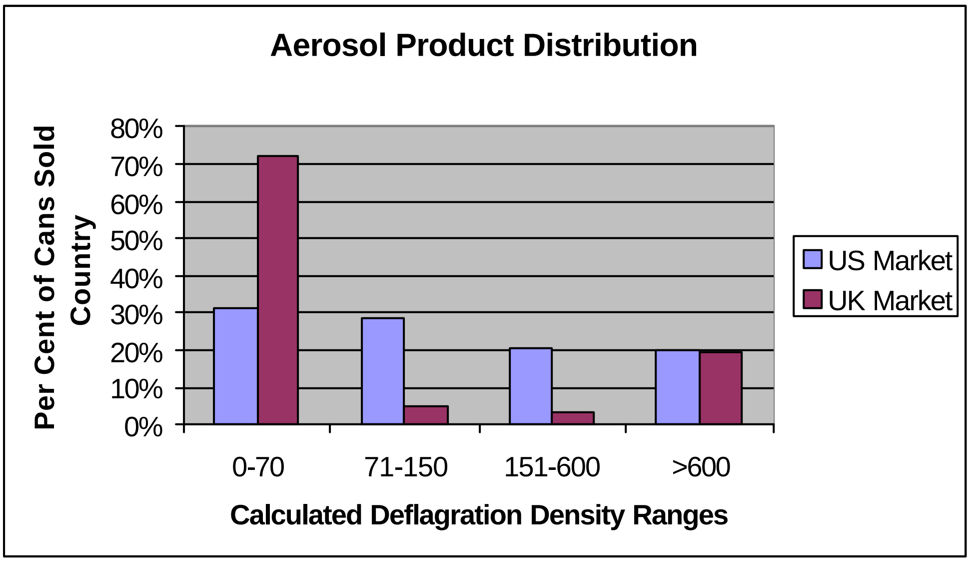
Table I

Ref. Number	Type of Product	Description	Chemical Heat of Combustion	Composite LEL by LEL Method	Visser's LEL Calculation Using Ch. Heat of Combustion	Calculated Deflagration Density- LEL method
			kJ/g	Volume %	Volume %	g/M3
3	Antiperspirant	Euro Style 84% HVOC	37	2.19	2.20	**51**
30	Penetrant/Lubricant	3% NF propellant	41	0.94	1.07	**51**
23	Insecticide	Wasp & Hornet	40	0.76	0.83	**52**
29	Engine Starter	ether & heptane	39	1.31	1.46	**54**
28	Engine Cleaner	Pre-VOC Controls	37	0.81	0.89	**55**
16	Air Freshener	Single-Phase Euro	34	2.65	2.70	**56**
6	Body Spray	Euro -High VOC	34	2.61	2.72	**58**
24	Insecticide	Crawling Bug- Solvent based	35	0.86	0.94	**59**
2	Antiperspirant	U.S. Style 60% HVOC	31	2.52	2.97	**72**
5	Deodorant	Euro Style 20% HC, balance EtOH	28	3.38	3.74	**74**
11	Hairspray	German Hairspray	24	4.08	4.04	**77**
8	Hairspray	80% VOC with 13% HCs	22	4.37	4.58	**89**
1	Antiperspirant	40% VOC- 40% HC, 20% FC	24	3.16	3.56	**90**
4	Deodorant	0% HVOC, 20% FC, high EtOH	21	4.42	4.45	**91**
7	Hairspray	80% VOC with DME, 15% water	20	7.04	6.83	**92**
27	Insecticide	Repellant	26	3.12	4.06	**96**
9	Hairspray	55% VOC with 152a, anhydrous	16	5.34	4.36	**96**
17	Disinfectant	NF propellant	20	4.88	5.44	**104**
12	Duster	All 152a	6	10.87	3.90	**107**
22	Insecticide	Water-based Fogger	16	4.52	4.54	**118**
26	Insecticide	Flying Insect	15	4.99	4.92	**124**
10	Hairspray	55% VOC with DME/Water	14	7.09	6.80	**130**
15	Air Feshener	30% VOC	13	6.49	6.40	**147**
25	Insecticide	Crawling Bug- Water based	9	9.07	9.23	**213**
32	Spray Wax	Water Out	6	11.10	11.63	**345**
14	Hair Mousse	16% VOC	5	16.81	16.92	**349**
19	Hard Surface Cleaner	General Purpose 10% VOC	8	7.03	10.16	**363**
20	Glass Cleaner	12% VOC	4	18.63	16.01	**383**
31	Spray Wax	Oil Out	9	9.06	19.12	**421**
18	Hard Surface Cleaner	Bathroom 7% VOC	5	15.56	29.67	**608**
21	Oven Cleaner	Oven Cleaner	5	15.52	26.33	**608**
13	Shave Foam	4% HC	2	52.02	49.92	**1040**

Table II

	Reference Number	Type of Product	Description	Calculated Deflagration Density	Measured Deflagration Density	MeasuredTime Equiv.	Ignition Distance	Flammable Content	Ch. Ht. of Combustion
A				g/M^3	g/M^3	s/M^3	cm	%	kJ/g
U	3	Antiperspirant	Euro Style 84% HVOC	51	50	85	nd	84	37
S	30	Penetrant/Lubricant	3% NF propellant	51	74	56	90	97	41
	8	Hairspray	80% VOC with 13% HCs	89	82	140	30	80	22
	1	Antiperspirant	40% VOC- 40% HC, 20% FC	90	80	117	nd	60	24
T	9	Hairspray	55% VOC with 152a	96	72	98	45	95	16
e	10	Hairspray	55% VOC with DME/Water	130	162	282	<15	53	14
s	7	Hairspray	80% VOC with DME	131	85	130	45	54	14
t	15	Air Feshener	30% VOC	147	154	215	<15	29	13
i	25	Insecticide	Crawling Bug- Water based	213	478	196	45	20	9
n	32	Spray Wax	Water Out	345	244	135	<15	13	6
g	18	Hard Surface Cleaner	Bathroom 6% VOC	716	>700	>700	<15	6	5
B									
E U									
t	16	Insecticide	Oil Based	45	nd	15	>45	100	43
e	14	Dry Air Freshener	90% prop	46	nd	74	<30	98	39
s	13	Body Spray	no water	61	nd	61	<45	98	32
t	11	Hairspray	50% prop; no water	72	nd	64	<45	96	27
i	9	Hairspray	40% prop; 40% water	117	nd	79	<45	60	13
n	15	Air Freshener	water based	136	nd	118	<30	50	13
g	21	Furniture Polish	33% flammables	155	nd	130	<15	33	13
		CSPA Proposals							
		Extremely Flammable			nd= no data				
		Flammable			note: EU ID test stopped at 45 cm				
		Non Flammable							

Chart


Aerosol Product Distribution
Per Cent of Cans Sold Country
80%
70%
60%
50%
40%
30%
20%
10%
0%
0-70
71-150
151-600
>600
Calculated Deflagration Density Ranges
US Market
UK Market