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SCIENTIFIC COMMITTEE ON CONSUMER PRODUCTS

SCCP

Opinion on

Clarifications to SCCNFP/0392/00 ‘An initial List of Perfumery Materials which must not form part of Cosmetic Products except subject to the Restrictions and Conditions laid down’

Adopted by the SCCP during the 8th plenary meeting
of 20 June 2006

Clarifications to SCCNFP/0392/00 ‘An initial List of Perfumery Materials which must not form part of Cosmetic Products except subject to the Restrictions and Conditions laid down’

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1. BACKGROUND

The SCCNFP¹ adopted at its 18th plenary meeting of 25 September 2001 the opinion SCCNFP/0392/00 ”An Initial List of Perfumery Materials which must not Form Part of Cosmetic Products except subject to the Restrictions and Conditions laid down”.

DG ENTR is in the process of implementing this opinion. The opinion is based on a list of IFRA restrictions. Some uncertainties have arisen during this work.

Entry 3 of the opinion foresees restrictions due to the possible content of allyl alcohol for the following 11 allyl esters:

<i>Allyl butyrate</i>	CAS n°: 2051-78-7
<i>Allyl cinnamate</i>	CAS n°: 1866-31-5
<i>Allyl cyclohexaneacetate</i>	CAS n°: 4728-82-9
<i>Allyl cyclohexanopropionate</i>	CAS n°: 2705-87-5
<i>Allyl heptanoate</i>	CAS n°: 142-19-8
<i>Allyl hexanoate</i>	CAS n°: 123-68-2
<i>Allyl isovalerate</i>	CAS n°: 2835-39-4
<i>Allyl octanoate</i>	CAS n°: 4230-97-1
<i>Allyl phenoxyacetate</i>	CAS n°: 7493-74-5
<i>Allyl phenylacetate</i>	CAS n°: 1797-74-6
<i>Allyl 3,5,5-trimethylhexanoate</i>	CAS n°: 71500-37-3

The opinion provides the following restriction: “*Use only when the level of free allyl alcohol in the ester is less than 0.1%.*” And is further said that the restriction is based on the delayed irritant potential of allyl alcohol (Food and Chemical Toxicology 15, 611 (1977)).

Allyl alcohol is classified as a toxic and irritant substance in directive 67/548/EEC.

Furthermore, in the scientific opinion (SCCNFP/0389/00) on sect II of the inventory perfumes and perfumery raw materials allyl esters are mentioned with the restrictions “Upper limit 0.1% of Allyl Alcohol as impurity”.

This opinion includes additional allyl esters to those mentioned in opinion SCCNFP/0392/00. (*allyl cyclohexyloxyacetate CAS 68901-15-5, allyl isoamyloxyacetate CAS 67634-00-8, allyl 2-methylbutoxyacetate CAS 67634-01-9, allyl nonanoate CAS 7493-72-3, allyl propionate CAS 2408-20-0 and allyl trimethylhexanoate CAS 68132-80-9*). Therefore a coherent approach regarding the 2 opinions should be followed.

Another problem in entries 4 and 23 of the SCCNFP opinion 0392/00 concerns allyl heptine carbonate, methyl octine carbonate and methyl heptine carbonate. (Methyl heptine carbonate is currently regulated in Annex III/1, 89 for labelling purposes). According to the opinion they are proposed to have restrictions of their final concentration in the finished cosmetic product due to their sensitising potential. However, these substances seem to belong to the group of alkyne

¹ Scientific Committee on Cosmetic Products and Non-Food Products intended for Consumers

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esters. “*Alkyne alcohols, their esters, ethers and salts*” are already regulated in annex II, entry 16 of the Cosmetic Directive for which no scientific opinion has ever been published.

2. TERMS OF REFERENCE

1. *Does the SCCP foresee the same restrictions for all the allyl esters mentioned in either 0392/00 or 0389/00? If yes, what restriction should be applied to these substances in the cosmetic products?*
2. *Does the SCCP consider that the use of allyl heptine carbonate, methyl octine carbonate and methyl heptine carbonate as fragrance ingredients is safe for the consumer?*

3. OPINION

3.1. Evaluation and Discussion

Regarding the first question:

In the opinion SCCNFP/0392/00 ”An Initial List of Perfumery Materials which must not Form Part of Cosmetic Products except subject to the Restrictions and Conditions laid down”, as well as in an Update of the initial list, adopted during the 26th Plenary meeting of 9 December 2003 (doc. n° SCCNFP/0770/03), it was stated that ‘*additional substances will be discussed for possible inclusion at a later date*’.

Both these opinions included only the substances for which a ‘monograph’ was available, listing them according to the names of the respective ‘monographs’ (not according to INCI names).

However, in a ‘Note on the allyl esters’ included in the related ‘monographs’ it is stated that “*a delayed type of irritation observed 2 or 3 days after exposure to allyl esters during human skin testing has caused the investigator to believe this to be a case of sensitisation. In every case these reactions have been traced to the presence of at least 0.1% of free allyl alcohol. While these esters are said to be quite stable, care should be exercised to obtain them as free as possible from this irritant alcohol. An extensive review of the safety evaluation of allyl esters from the point of view of their use in flavourings has been made by Drake (1975)*”.

Despite the confused and inappropriate terminology used in the above and taking also into account that these esters are expected to be readily hydrolysed in the skin, liberating allyl alcohol, in the “Scientific opinion on section II of the inventory - perfumes and perfumery raw materials (doc. n° SCCNFP/0389/00), the same restrictions were considered to be applicable to all allyl esters listed in section II of the inventory.

The SCCP draws attention to the possibility that allyl esters may be hydrolysed in the skin to allyl alcohol, but is not considered here because of the absence of relevant data.

In conclusion, the following six esters of allyl alcohols should be added to the initial list of allyl esters that may be used as ingredients in cosmetic products only under the conditions and restrictions previously specified for allyl esters.

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<i>Allyl Cyclohexyloxyacetate</i>	CAS 68901-15-5
<i>Allyl Isoamyloxyacetate</i>	CAS 67634-00-8
<i>Allyl 2-Methylbutoxyacetate</i>	CAS 67634-01-9
<i>Allyl Nonanoate</i>	CAS 7493-72-3
<i>Allyl Propionate</i>	CAS 2408-20-0
<i>Allyl Trimethylhexanoate</i>	CAS 68132-80-9

Regarding the second question:

The old terms “heptine carbonate” and “octine carbonate” are used in INCI names as synonyms of “2-octynoate” and “2-nonynoate” respectively, i.e. to organic acid derivatives having a triple bond located in the position 2 of their ‘acyl’ moiety (apparently, the location of triple bond is omitted in the INCI name for reasons of simplicity).

Examples of Esters of Alkynoic Acids									
Methyl 4-Alkynoate (or Methyl Alk-4-ynoate) [Methylester of an alkynoic acid having a triple bond starting at C-4 (at the position 4) of the acyl moiety]						$\begin{array}{ccccccc} & 5 & 4 & 3 & 2 & 1 \\ \text{CH}_3-(\text{CH}_2)_n-\text{C}\equiv\text{C}-\text{CH}_2\text{CH}_2-\text{C}=\text{O}-\text{CH}_3 \\ & (4\text{-alkynoate}) & & & & & (\text{methyl}) \end{array}$			
Methyl 2-Octynoate (or Methyl Oct-4-ynoate) INCI name : Methyl Heptine Carbonate						$\begin{array}{ccccccc} & 8 & 7 & 6 & 5 & 4 & 3 & 2 & 1 \\ \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2-\text{C}\equiv\text{C}-\text{C}=\text{O}-\text{CH}_3 \\ & (2\text{-octynoate}) & & & & & & (\text{methyl}) \end{array}$			
Allyl 2-Octynoate (or 2-Propenyl Oct-4-ynoate) INCI name : Allyl Heptine Carbonate						$\begin{array}{ccccccc} & 8 & 7 & 6 & 5 & 4 & 3 & 2 & 1 & 1' & 2' & 3' \\ \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2-\text{C}\equiv\text{C}-\text{C}=\text{O}-\text{CH}_2\text{CH}=\text{CH}_2 \\ & (2\text{-octynoate}) & & & & & & & & & & (\text{allyl or 2-propenyl}) \end{array}$			
Methyl 2-Nonynoate (or Methyl Non-4-ynoate) INCI name : Methyl Octine Carbonate						$\begin{array}{ccccccc} & 9 & 8 & 7 & 6 & 5 & 4 & 3 & 2 & 1 \\ \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2-\text{C}\equiv\text{C}-\text{C}=\text{O}-\text{CH}_3 \\ & (2\text{-nonynoate}) & & & & & & & & (\text{methyl}) \end{array}$			

The entry 16 of annex II of the Cosmetic Directive refers to “alkyne alcohols” and to “esters or ethers or salts of alkyne alcohols”. According to the IUPAC and CAS rules of chemical nomenclature, these alcohols are named ‘alkynols’ or ‘alkynyl (alkinyl) alcohols’, and their esters or ethers are named ‘alkynyl esters’ and ‘alkynyl ethers’ respectively.

Examples of Alkynyl Alcohols and their Esters and Ethers									
3-Octynol or 3-Octynyl alcohol or Oct-3-ynyl alcohol (having a triple bond starting at carbon atom C-3, i.e. at the position 3 of the hydrocarbon chain)					8	7	6	5	4
					3	2	1		
					$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2 - \text{C}\equiv\text{C} - \text{CH}_2\text{CH}_2\text{-OH}$				
2-Propynyl 3-Pentenoate or Prop-2-ynyl Pent-3-enoate or 3-Pentenoic acid, 2-propynyl ester					5	4	3	2	1
					1'	2'	3'		
					$\text{CH}_3\text{CH}=\text{CHCH}_2 - \underset{\text{O}}{\overset{ }{\text{C}}} - \text{O} - \text{CH}_2 - \text{C}\equiv\text{CH}$				
					(3-pentenoate)	O	(2-propynyl)		
3-Pentenyl 2-Propynyl Ether					5	4	3	2	1
					1'	2'	3'		
					$\text{CH}_3\text{CH}=\text{CHCH}_2 - \text{C}\equiv\text{CH} - \text{O} - \text{CH}_2 - \text{C}\equiv\text{CH}$				
					(3-pentenyl)		(2-propynyl)		

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As shown in the above examples, the triple bond (denoted by the “yn”) occurs in a hydrocarbon chain not containing a carboxy-group, as in the previous case of alkynoic acids and their esters. Therefore, the group of alkynyl esters (see note below) is quite distinct from the group of esters of alkynoic acids, and allyl heptine carbonate, methyl octine carbonate and methyl heptine carbonate do not belong to the alkynyl esters regulated by the entry 16 of annex II of the Cosmetic Directive.

Note: As mentioned, the terms “alkyne alcohols” and “alkyne esters” do not comply with chemical nomenclature rules of IUPAC or CAS. However, in the first case there is no controversy; e.g. using the name “propyne alcohol” instead of “propynyl alcohol” resembles to using the name “ethane alcohol” instead of “ethyl alcohol”. On the opposite, the term “propyne esters” (used in the mandate) is controversial because it is not synonymous to “propynyl esters” and may be interpreted as including also the esters of propynoic acids (first group defined above), just as it happened in the second question of the present mandate.

Conclusion

The current regulations regarding allyl heptine carbonate, methyl octine carbonate and methyl heptine carbonate are not contradictory to the regulations related to allyl alcohol and allyl esters.

4. REFERENCES

1. Opinion of the Scientific Committee on Cosmetic Products and Non-Food Products intended for Consumers concerning an initial list of perfumery materials which must not form part of cosmetic products except subject to the restrictions and conditions laid down. Adopted by the SCCNFP during the 18th plenary meeting of 25 September 2001 - Doc. n° SCCNFP/0392/00.
2. Opinion of the Scientific Committee on Cosmetic Products and Non-Food Products intended for Consumers concerning the 1st Update of the inventory of ingredients employed in cosmetic products - Section II: Perfume and Aromatic raw materials Adopted by the SCCNFP during the plenary session of 24 October 2000 - Doc. n° SCCNFP/0389/00.

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