Survey of Chemical Substances in Consumer Products

Survey no. 20, 2003

Investigation of chemical substances in products containing decorative liquids

Birgit Lundskov, Anne Dilani Pedersen, Erik Andersen

Danish Technological Institute, Chemical Department

Danish Environmental Protection Agency

Danish Ministry of the Environment

Contents

Summary

16 products containing decorative liquids have been purchased by the Danish Environmental Protection Agency and they have been analysed by the Chemical Department at Danish Technological Institute.

In the samples with 2-phase liquids, the coloured liquids have been identified as water and the colourless liquids have been identified as different mineral oils. The oils consist of hydrocarbons in the interval C_8H_{18}-$C_{26}H_{54}$.

In three of the samples a content of phthalates was found; DPB (dibutyl phthalate and DEHP (bis(2(-ethylhexyl)phthalate). These plasticizers might originate from the plastic container.

In three of the samples bactericidal substances called methyl-isothiazolinone and chloro-methyl-isothiazolinone, respectively, were found.

The dyes were identified as triarylmethane dye (patent blue VF) and monoazo dyes (Sunset Yellow, Tartrazin, Ponceau 4R, Red 2G and Acid red 33).

In the aqueous phase, two samples contain 89-95 g/L sodium chloride and one sample contains 503 g/L calcium chloride.

Qualitative screening analysis showed a content of xylen and trimethylbenzen in three of the samples and cyclohexanone, cyclohexanol and butoxyethanol in four of the samples. The analysis also showed a content of decahydronaphtalin in 2 of the samples.

Cinematic viscosity measurements were carried out on selected oils. All oils are characterised as being low viscosity oils.

Sammenfatning

Miljøstyrelsen har indkøbt 16 produkter indeholdende dekorative væsker. Produkterne er analyseret af Teknologisk Institut, Kemiteknik.

I produkter med 2 faser er de farvede faser identificeret som vand og de farveløse faser som forskellige mineralske olier. Olierne består af kulbrinter i intervallet C_8H_{18}-$C_{26}H_{54}$.

I 3 af prøverne er der fundet indhold af phthalater; dibutyl phthalat (DBP) og bis(2-ethylhexyl) phthalat (DEHP). Disse blødgørere kan stamme fra plastmaterialet.

I 3 af prøverne er der fundet konserveringsmidler, henholdsvis methyl-isothiazolinon og chloro-methyl-isothiazolinon.

Farvestofferne er identificeret som triarylmethan farvestof (patentblå VF) og monoazo farvestoffer (sunset yellow, tartrazin, ponceau 4R, red 2G og acid red 33).

To prøver indeholder, i vandfasen, 89-95 g/L natriumchlorid og 1 prøve indeholder 503 g/L calciumchlorid.

Ved kvalitativ screening er der fundet indhold af xylener og trimethylbenzener i 3 prøver og cyklohexanon, cycklohexanol og butoxyethanol i 4 prøver. Der kan desuden nævnes indhold af decahydronaphtalin i 2 prøver.

Der er foretaget kinematisk viskositetsmålinger på udvalgte oliefaser. Alle karakteriseres som værende af lav viskositet.

1 Background and objective

The objective of this project is to investigate which chemical substances exist in products in the Danish market that contain decorative liquids.

The Danish Environmental Protection Agency has implemented this investigation which together with a number of other projects will assess the content of chemical substances in consumer products.

There is a risk that these liquids somehow might leak and that children might get into touch with them and therefore it is relevant for consumers to receive information about which chemicals they risk being exposed to.

16 different products containing decorative liquids have been examined.

- Eleven products contain a colourless and a coloured liquid.
- Four products contain one coloured liquid.
- One product differs from the others as it – beyond an aqueous phase – also contains a viscous phase.

All products are embedded in plastic material.

The investigation is solely based on chemical analyses, as the distributors were not in possession of any product information from the manufacturers.

2 Description of products

The Danish Environmental Protection Agency has purchased 16 different products containing decorative liquids. The products are described in table 1.

Table 1: Product specification

Sample number	Product specification
1.	Tooth mug with two liquid phases, clear-blue.
2.	Holder for tooth brushes with two liquid phases, clear-blue.
3.	Soap dish with two liquid phases, clear-blue.
4.	Shower curtain with a blue liquid with a little stardust.
5.	Paper weight with one clear liquid with stardust.
6.	Torpedo (for decoration) with four chambers with 2 liquid phases in each chamber: clear-blue, clear-green, clear-pink, clear-red.
7.	Bottle opener with two liquid phases, clear-pink.
8.	Bottle opener with two liquid phases, clear-light blue.
9.	Bottle opener with two liquid phases, clear-lilac.
10.	Bottle opener with two liquid phases, clear-orange.
11.	Hourglass with two liquid phases, clear-yellow/orange.
12.	Hourglass with two liquid phases, clear-pink.
13.	Glass with a coloured liquid.
14.	Lamp with blue liquid and red solid phase that becomes fluid when the lamp is switched on.
15.	Lamp with blue liquid and stardust that is in motion when the lamp is switched on.
16.	Keyring with two liquid phases; clear-blue.

3 Methods of analysis

Before the products are analysed the liquids are removed from the different products. That takes place by boring a hole in the plastic material. In cases where there are 2 liquid phases, the phases are separated. Solubility tests are carried out with dichloromethane to investigate to which extent the liquids are polar (mixable with water) or non-polar before the analyses are started.

In order to carry out quantitative and qualitative analyses of the samples, the below techniques have been used:

1. Identification of the liquid phases through gas chromatography with flame ionisation detector (1. GC-FID) and infrared spectrometry (2. IR).
2. Identification and quantification of organic additives through gas chromatography with mass spectrometric detection (3. GC-MS).
3. Identification of dyes through thin layer chromatography (4. TLC) and liquid chromatography (5. HPLC).
4. Identification and quantification of inorganic additives through X-ray fluorescence spectrometry (6. EDXRF) and ion chromatography (7. IC – DS/EN ISO 10304-2).
5. Determination of cinematic viscosity according to ASTM D445.

3.1 Identification of liquid phases through gas chromatography with flame ionisation detector (GC-FID) and infrared spectrometry (IR)

The oil phases are diluted with methylene chloride to which bromobenzene and o-terphenyl have been added as internal standards. The fixed phase in sample 14 is dissolved in carbon disulphide. The dilutions and the wax solution are analysed gas chromatographically with flame ionisation detector (GC-FID). The methods used to analyse the oil phases have in the following been marked with 1. The methods used to analyse the wax solution have in the following been marked with 2.

GC-FID:	HP 5890
Column:	**1**. Cpsil 5CB L(25m), Ft(0.25µm), Id(0.25mm) and **2**. CPsil 5 L(5m), Ft(0.25µm), Id(0.32mm) (for wax)
Temperature program:	**1**. 40°C (0 min)- 12°C/min- 125°C (0 min) – 285°C (20 min) and **2**. 100°C (0min) - 10°C/min – 290°C(30min)
Injection temperature:	**1**. 250°C, **2**. 300°C
Injection type:	**1**. + **2**. Liner with glowing glass wool

In order to determine the hydrocarbon composition and the boiling point interval, known mineral oil products and hydrocarbon standard series from C_8H_{18} to $C_{35}H_{72}$ and $C_{20}H_{42}$ to $C_{44}H_{90}$ are analysed.

The water phases are identified through fourier transform infrared spectrometry by using potassium bromide technology. A thin layer of the liquid is placed on a potassium bromide tablet and IR spectrum is taken on a Perkin Elmer 1720x FT-IR spectrometer. Examples of the IR spectra of a water phase and a mineral oil phase appear from enclosure B.

3.2 Identification and quantification of organic additives through gas chromatography with mass spectrometric detection, GC-MS

The oil phases are diluted with methylene chloride to which bromobenzene and o-terphynyl have been added as internal standards. The water phases are extracted with methylene chloride to which the same internal standards have been added. The dilutions and extracts are analysed gas chromatographically with mass spectrometric detection. In order to identify individual components MS NIST98 library search is applied.

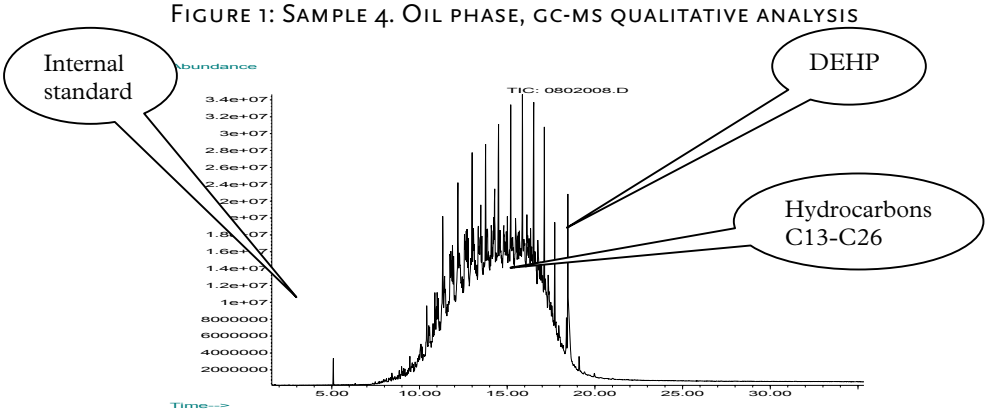
GC-MS : HP 5890
Column : VB-1 L(30m), Ft(0.5µm), Id(0.32mm)
Temperature program : 35°C(1 min)-15°C/min - 280°C (18min)
Injection temperature : 35°C

In connection with GC-MS screening the additives are identified as phthalates and bactericidal substances. The content of bactericidal substances is determined semi-quantitatively against the internal standard, bromobenzene, as it was not possible to obtain the reference standards. Bromobenzene is used routinely as internal standard in the boiling point area in which the bactericidal substances are situated. The content of phthalates is determined quantitatively against external standards. In table 2, the detection limits are stated. In figure 1, there is an example of chromatogram of the oil phase in sample 4.

Table 2: Detection limits

Parameters	Determination	Phase	Detection limit
Individual component	Qualitative	Water	1-100 µg/mL
		Oil	50-500 µg/mL
Phthalates	Quantitative	Water	0.05 µg/mL
Bactericidal substances	Semi-quantitative	Water	1 µg/mL

Figure 1: Sample 4. Oil phase, gc-ms qualitative analysis



3.3 Identification of dyes through thin layer chromatography (TLC) and liquid chromatography (HPLC)

TLC is used for the initial comparison of dyes. The samples are evaporated to dryness and decomposed once again in water. Sodium citrate (5% NH_3)

is used as elution liquid and the applied TLC plates are coated with cellulose. For final identification HPLC is used with UV diode array detector and a number of reference colours used within the food industry are included.

HPLC:	HP 1100
Column:	Phenomenex Luna C_8 L(15cm), grain size (5µm), Id(4.6mm)
Mobile phase:	Acetonitril and 0.01 M natrium perchlorate, pH is set at 3.0 with perchloric acid
Injection volume:	10 µL

Chromatograms are taken by means of screening and at selected wave lengths: 254 nm, 430 nm, 520 nm and 640 nm, see table 3.

The samples are "washed" with hexane to remove possible oil residues, they are evaporated to dryness and decomposed once again in mobile phase. Samples that cannot be evaporated are analysed directly on HPLC. In order to identify dyes they are compared with reference dyes and the table in ref (1). Enclosure C gives examples of UV curves. Ref (2) is used as reference of colours.

Table 3: Wave lengths and colours

Wave lengths in nm	Colours
254	All
430	Yellow
520	Red
640	Blue/green

3.4 Identification and quantification of inorganic additives through X-ray fluorescence spectrometry (EDXRF) and ion chromatography (IC)

EDXRF screening has been carried out on oil, water and solid-state fractions. Liquids are transferred to Somar Cups with mylar foil and analysed on a PV9100 spectrometer with helium in the test chamber. Through this technique the samples can be screened for elements on and after atomic number 14 (silicium). Lighter elements do not appear with this technology.

Precipitates, stardust etc. have been filtered off, washed out for oil and analysed under vacuum. In that way, it is possible to analyse down to atomic number 11 (sodium). The detection limit is 0.1 w/w%.

Proven salts are determined quantitatively through ion chromatographical analysis with a 2.7 mM Na_2CO_3 and 1.0 mM $NaHCO_3$ solution as elution liquid.

3.5 Determination of cinematic viscosity

Cinematic viscosity measurements have been carried out at 40 °C on 7 oil phases. They were carried out by the sub-supplier ITS Caleb-brett, Dokhavnsvej 3, P.O. Box 67, DK-4400 Kalundborg.

The applied method is ASTM D 445, which is analogous with the ISO 3104 method. During theses measurements gravitation was used as the motive power on the liquid and in that way the density of the liquid forms part of the calculation. The measurements are carried out by setting a fixed amount of liquid in circulation, letting it run out of a nozzle and then measuring time. The results are stated in m^2/sec.

4 Results

In this chapter the following results are studied: Identification of liquids and dyes by means of IR, GC-FID, HPLC and TLC, determination of additives by means of GC-MS, EDXRF and IC and cinematic viscosity measurements

4.1 Identification of liquids and dyes

The liquids have been identified as water and mineral oils consisting of hydrocarbons in the interval of C_8H_{18}-$C_{26}H_{54}$, corresponding to the boiling point interval of 126°C-412°C.

The solid substance in sample 14, has been identified as wax consisting of hydrocarbons $C_{20}H_{42}$-$C_{44}H_{90,}$, corresponding to the boiling point interval of 343°C-548°C. The analysis results appear from table 4. In enclosure D there is a list with CAS numbers on identified hydrocarbons.

In enclosure A, selected chromatograms are shown to illustrate the different composition of hydrocarbons in oil.

The dyes have been identified as triarylmethane dye (patent blue VF) and monoazo dyes (sunset yellow, tartrazin, ponceau 4R, red 2G and acid red 33).

Table 4: Hydrocarbon interval and dyes

Sample number	No. Of phases	Oil phase Hydrocarbon interval	Colour of oil phase	Boiling point interval	Water phase	CI no.	Colour of water phase
Method		1		1	4 and 5		
1.	2	C13-C26	Colourless	235-412°C	Patent blue VF	42045 (blue)	Blue
2.	2	C13-C26	Colourless	235-412°C	Patent blue VF	42045 (blue)	Blue
3.	2	C13-C26	Colourless	235-412°C	Patent blue VF	42045 (blue)	Blue
4.	1	C13-C26 Dye not identified	Blue	235-412°C	None	-	None
5.	1	None	-	None	Dye not identified	-	Pink
6.	5	C11-C21	Colourless	196-356°C	Patent blue VF Tartrazin	42045 (blue) 19140 (yellow)	Green
			Colourless		Patent blue VF	42045 (blue)	Blue
			Colourless		Presumably[2] Acid Red 33	17200 (red)	Pink
			Colourless		Ponceau 4R	16255 (red)	Red
7.	2	C13-C21	Colourless	235-356°C	Presumably[2] Red 2G	18050 (red)	Pink
8.	2	C8-C21	Colourless	126-356°C	Patent blue VF	42045 (blue)	Light blue
9.	2	C8-C21	Colourless	126-356°C	Patent blue VF + presumably[2] Red 2G	42045 (blue) 18050 (red)	Lilac
10.	2	C8-C21	Colourless	126-356°C	Patent blue VF	42045 (blue)	Orange
11.	2	C12-C15	Colourless	216-271°C	Sunset Yellow	15985 (orange)	Yellow
12.	2	C12-C15	Colourless	216-271°C	Presumably[2] Red 2G	18050 (red)	Pink
13.	1	None	-		Ponceau 4R Tartrazin + presumably[3] Patent blue VF	16255 (red) 19140 (yellow) 42045 (blue)	Brandy
14.	2	C20-C44[1]	Red[1]	344-548°C	Dye not identified	-	Blue
15.	1	None	-		Dye not identified	-	Lilac/blue
16.	2	C13-C21	Colourless	235-356°C	Patent blue VF	42045 (blue)	Blue

[1] This sample contains a solid red wax phase and a blue water phase.

[2] Identification was carried out by comparing the UV spectrum with absorption maxima in the table in ref. 1, page 19, and not by comparison with reference dye.

[3] Identification is solely carried out by comparing the retention time of the reference dye and blue dye in sample. The UV spectrum of the blue dye in the sample could not be absorbed as the signal was too small.

4.2 Additives

In some tests additives such as salts, bactericidal substances and phthalates, bis(2-ethylhexyl)phthalate (DEHP) and dibutyl phthalate (DBP) were demonstrated in the water phase. It cannot be ruled out that the phthalates originate from the plastic material. Salts have probably been added in order to change the density so the items can float. In table 5, all the results have been collected. The detection limits are stated in table 2.

Table 5: Additives

Sample number	DEHP mg/mL	DBP mg/mL	CaCl2 mg/mL	NaCl mg/mL	Methyl-isothiazolinon mg/mL	Chloro-methyl-isothiazolinon mg/mL
CAS no.	117-81-7	84-74-2	10043-52-3	7647-14-5	2682-20-4	26172-55-4
Method	3	3	7	7	3	3
4.	18	-	-	-	-	-
5.	-	-	-	-	0.002	0.02
6b. blue phase	-	-	-	-	0.04	0.14
6d. red phase	-	-	-	-	0.01	0.07
8.	0.25	-	-	-	-	-
9.	-	-	-	89	-	-
10.	-	-	-	95	-	-
15.	-	0.02	500	-	-	-

- means not proven

In samples 7, 8, 9 and 10 which is the same type of product, DEHP only exists in one and NaCl exists in two of the products. The content of DEHP is probably from the plastic material, which is soft plastic and probably soft PVC. However, it cannot immediately be explained why salt has been added to sample 9 and 10.

In table 6, there is a list of the substances that have been found qualitatively through the GC-MS screening. Identification has solely been carried out by comparing with the MS Nist reference library and therefore isomeric combinations might be in question.

Table 6: List of contents determined qualitatively through GC-MS screening. Detection limit 1-100 µg/mL (water phase) and 50-500 µg/mL (oil phase)

Sample number	Oil phase			Water phase		
	Component	µg/mL	Detection limit µg/mL	Component	µg/mL	Detection limit µg/mL
Method	3			3		
1.	-			Cyclohexanone Cyclohexanol 2-Butoxyethanol	< 10	1
2.	-			Cyclohexanone Cyclohexanol 2-butoxyethanol	<10	1
3.	-			-		
4.	-			No water phase		
5.	No oil phase			Butanol Methyl benzen sulphonamides	<5	1
6.	-			Green: Cyclohexanone Butoxyethanol	<5	1
				Blue: -		
				Pink: Cyclohexanone Butoxyethanol	<5	1
				Red: -		
7.	-			-		
8.	Xylenes Trimethylbenzenes	<1200 <2500	50	Xylenes Trimethylbenzenes	<10	1
9.	Xylenes Trimethylbenzenes	<1200 <2500	50	Xylenes Trimethylbenzenes	<10	1
10.	Xylenes Trimethylbenzenes	<1200 <2500	50	Xylenes Trimethylbenzenes	<10	1
11.	Trans+cis, decahydronaphthalene *	<10000	500	Trimethylbenzenes Trans+cis, decahydronaphthalene *	< 50	10
12.	Trans+cis, decahydronaphthalene *	<10000	500	Trans+cis, decahydronaphthalene *	<50	10
13.	No oil phase			-		
14.	No oil phase			1.3 dimethoxy-2-propanol 2-butoxyethanol Alkylbenzenes	<5 <5 <100	1 1 10
15.	No oil phase			-		
16.	-			Propylene glycol 2 butoxyethanol 2-(2-butoxyethoxy) ethanol	<100 <50 <5	10 1 1

* CAS no. 91-17-8

\- means no qualitative determination

The content of components in the oil phase is of the magnitude as can be seen in the table. The content of xylenes in the oil phase is e.g. 50-1200 µg/mL.

4.3 Cinematic viscosity

Cinematic viscosity has been measured in 7 of the products. The viscosity was measured because a very low viscosity can cause chemically-induced pneumonia.

7 products have been selected where the cinematic viscosity of the oil phase was measured at 40°C, during sub-delivery. All 7 oil phases are characterised as light oils, i.e. they have low viscosity.

Table 7: Viscosity measurements on oil phases in cSt (= 10^{-6} m^2/sec)

Sample number	Viscosity at 40 °C
1.	10.3
2.	10.3
3.	10.3
6.	5.36
7.	3.42
11.	2.48
16.	15.9

Reference List

1 Identification of cosmetic dyes by ion-pair reversed-phase high-performance liquid chromatography, journal of chromatography, 394 (1987), 345-352

2 Colouring of foods, drugs and cosmetics, Gilbert Otterstätter, Marcel Dekker, inc. 1999

Enclosure A: Illustration of the different compositions of hydrocarbons in oil

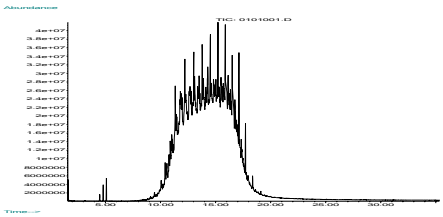


Figure 2: Product 1.

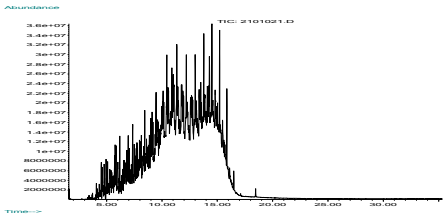


Figure 3: Product 8.

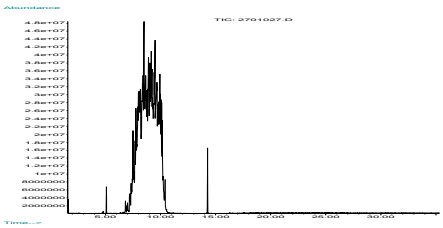


Figure 4: Product 11.

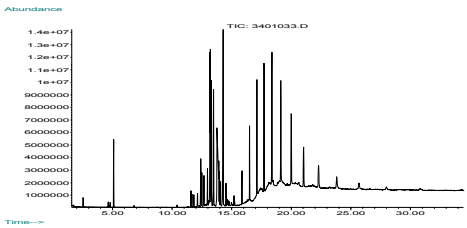


Figure 5: Product 14.

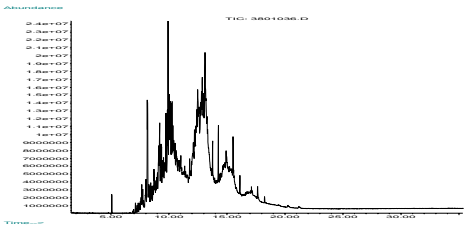


Figure 6: Product 16.

Figure 7-9: 3 different oils

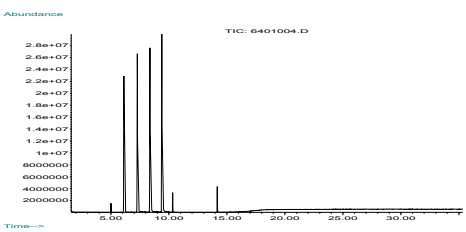


Figure 7: Borup Lamp oil

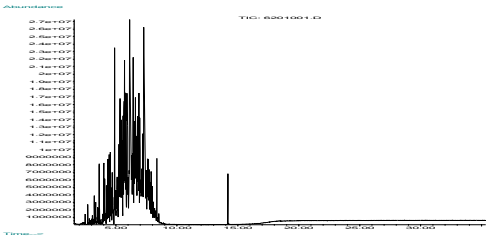


Figure 8: Turpentine

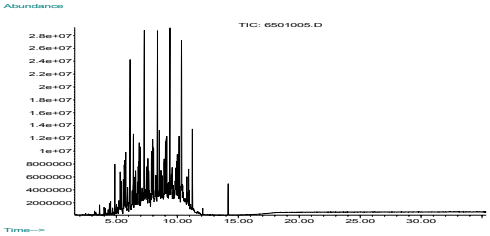


Figure 9: Petroleum

Enclosure B: Examples of IR spectra

Figure 10: Product 1 water phase.

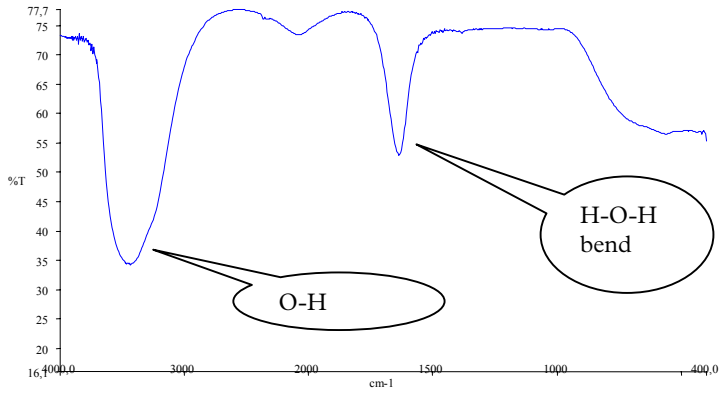
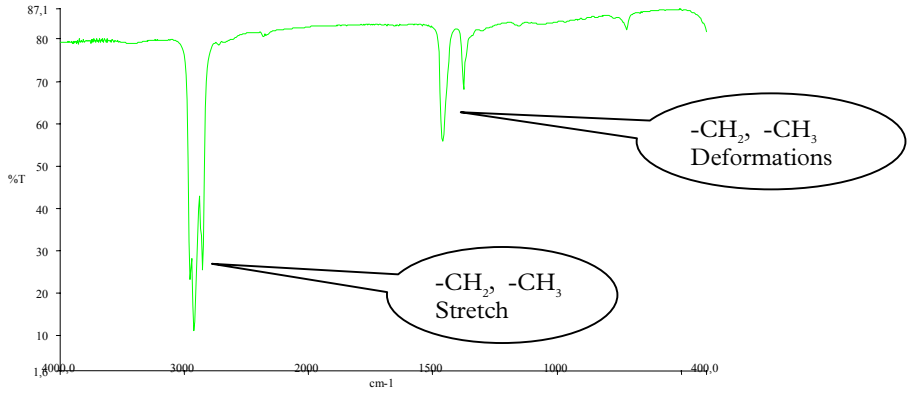


Figure 11: Product 1, oil phase



Enclosure C: Examples of UV spectra of dyes

Figure 12: UV Spectra of CI 16255 (Ponceau 4R)

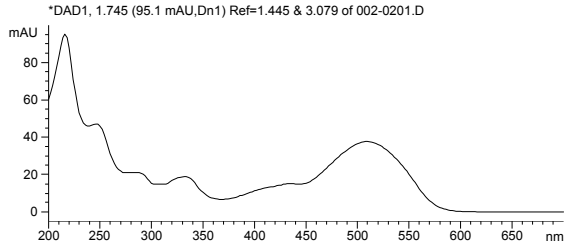


Figure 13: UV spectra of product 6d, red water phase. Identified as CI 16255 (Ponceau 4R)

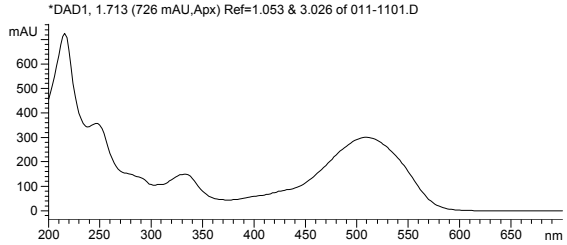


Figure 14: UV spectra of CI15985 (Sunset Yellow)

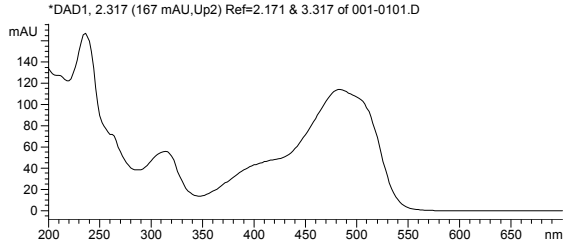
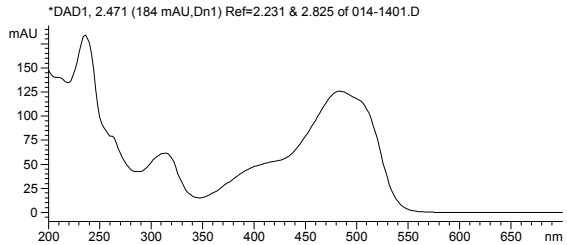


Figure 15: UV spectra of product 11. Yellow water phase. Identified as CI15985 (Sunset Yellow)



Enclosure D: CAS numbers on identified hydrocarbons

Sample number	Oil phase hydrocarbon interval
1.	C13-C26
2.	C13-C26
3.	C13-C26
6.	C11-C21
7.	C13-C21
8.	C8-C21
11.	C12-C15
14.	C20-C44
16.	C13-C21

C_nH_{2n+2}	CAS no.
C_8H_{18}	11-65-9
C_9H_{20}	111-84-2
$C_{10}H_{22}$	124-18-5
$C_{11}H_{24}$	1120-21-4
$C_{12}H_{26}$	112-40-3
$C_{13}H_{28}$	629-50-5
$C_{14}H_{30}$	629-59-4
$C_{15}H_{32}$	629-62-9
$C_{16}H_{34}$	544-76-3
$C_{17}H_{36}$	629-78-7
$C_{18}H_{38}$	593-45-3
$C_{19}H_{40}$	629-92-5
$C_{20}H_{42}$	112-95-8
$C_{21}H_{44}$	629-94-7
$C_{22}H_{46}$	629-97-0
$C_{23}H_{48}$	368-67-5
$C_{24}H_{50}$	646-31-1
$C_{25}H_{52}$	629-99-2
$C_{26}H_{54}$	630-01-3
$C_{27}H_{56}$	593-49-7
$C_{28}H_{58}$	630-02-4
$C_{29}H_{60}$	630-03-5
$C_{30}H_{62}$	628-68-6
$C_{31}H_{64}$	630-04-6
$C_{32}H_{66}$	544-85-4
$C_{33}H_{68}$	630-05-7
$C_{34}H_{70}$	14167-59-0
$C_{35}H_{72}$	630-07-9
$C_{36}H_{74}$	630-06-8
$C_{37}H_{76}$	-
$C_{38}H_{78}$	7194-85-6
$C_{39}H_{80}$	-
$C_{40}H_{82}$	4181-95-7
$C_{41}H_{84}$	-
$C_{42}H_{86}$	7098-20-6
$C_{43}H_{88}$	-
$C_{44}H_{90}$	7098-22-8