

ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE
ENGINEERING AND TECHNOLOGY

**INVESTIGATION OF SOME ADDITIVES USED IN THE PRODUCTION OF
POLYMER CONTAINING MATERIALS**

M.Sc. THESIS

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Department of Polymer Science and Technology

Polymer Science and Technology Programme

JANUARY 2012

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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

**POLİMER İÇERİKLİ MALZEME ÜRETİMİNDE KULLANILAN BAZI
KATKI MALZEMELERİNİN İNCELENMESİ**

YÜKSEK LİSANS TEZİ

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To my mum and dad,

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January 2012

Hale TOZLU
Chemical Engineer

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ABBREVIATIONS

| | |
|--------------|---|
| BB | : Benzyl benzoate |
| BBP | : Benzyl butyl phthalate |
| BCC | : Business Communication Company |
| CI | : Chemical ionization |
| CMR | : Carcinogenic, mutagenic and reprotoxic |
| DBP | : Dibutyl phthalate |
| DCM | : Dichloromethane |
| DEHP | : Bis (2-ethylhexyl) phthalate |
| DIBP | : Diisobutyl Phthalate |
| DIDP | : Diisodecyl phthalate |
| DINP | : Diisononyl phthalate |
| DNOP | : Di-n-octylphthalate |
| DSC | : Differential scanning calorimetry |
| ECHA | : European Chemicals Agency |
| EPS | : Expanded polystyrene |
| EU | : European Union |
| FID | : Flame ionization detector |
| FSWC | : Fused-silica wall-coated |
| FTIR | : Fourier transform infrared spectroscopy |
| GC/MS | : Gas Spectroscopy / Mass Spectrometry |
| HBCDD | : Hexabromocyclododecane |
| HPLC | : High-performance liquid chromatography |
| IS | : Internal Standard |
| PBT | : Persistent bioaccumulative toxic |
| PS | : Polystyrene |
| PU | : Polyurethane |
| PVC | : Poly (vinyl) chloride |
| REACH | : Registration, Evaluation, Authorization and Restriction of Chemicals |
| SCOT | : Support-coated open tubular |
| SIC | : Single-ion chromatogram |
| SIM | : Selective Ion Monitoring |
| SVHC | : Substances of Very High Concern |
| TGA | : Thermogravimetric Analysis |
| THF | : Tetrahydrofuran |
| TIC | : Total-ion chromatogram |
| UPLC | : Ultra-performance liquid chromatography |
| vPvB | : Very persistent very bioaccumulative |
| WCOT | : Wall-coated open tubular |

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INVESTIGATION OF SOME ADDITIVES USED IN THE PRODUCTION OF POLYMER CONTAINING MATERIALS

SUMMARY

Many things that we see around us and use are polymers. Polymers used in production of very kind of materials. Several parts of white appliances and consumer electronics have also contained polymeric materials.

Polymers contain auxiliaries for essential functional properties; each should be used in optimum amounts for attainment of high-quality products. These auxiliaries are subdivided into additives and modifiers. Additives are used in small proportions and modifiers are added in greater proportions. Additives do not affect mechanical properties but modifiers modify mechanical properties. Both additives and modifiers are combined with polymers after the polymerization. Sometimes, they aid processing (process additives) or sometimes they improve usage properties of polymers (functional additives and modifiers). Plasticizers, antioxidants, heat and UV stabilizers, flame retardants, colorants, fillers are the main polymer auxiliaries. Compatibility and miscibility of additives with the polymers are very important and limit the amount of the additives. Without additives, plastics would not work, but with them plastics can be made safer, cleaner, tougher, and more colorful.

According to BCC Inc. report; 2.7 million tons of plastics additives were used in Europe in 2006. Plasticizers dominate the market, representing some 56% of the market. Flame retardants are the second largest market segment.

Plasticizers are polymer additives that serve to increase the polymer's flexibility, elongation and ease of processing. Phthalates command the plasticizers market due to their low cost, ease of use and availability. Other common plasticizers include adipates, polymeric and trimellitates.

Over 90 percent of plasticizer volume goes into flexible PVC applications. Plasticizer can be mixed with PVC in all portions so plasticized PVC polymer is found in a wide variety of products including white appliances and consumer electronics.

REACH is a European chemicals and substance regulation that applies to nearly all products that are manufactured or imported into the European Union (including European Economic Area (EEA) countries). The acronym REACH stands for: Registration, Evaluation, Authorization and Restriction of Chemicals. It is a complex regulation (Regulation (EC) No 1907/2006) consolidating over 40 previous legislations under one umbrella and adding many new requirements.

The European REACH regulation imposes requirements to declare and sometimes restrict the use of Substances of Very High Concern (SVHC) because of their hazardous properties: Carcinogenic, Mutagenic, Toxic for reproduction etc. REACH affects all product types and forces the home appliances and consumer electronics industry to investigate these substances.

The SVHC list includes polymer performance chemicals such as plasticizers, flame retardants, and various functional additives added intentionally or as contaminants due to the use of recyclates. Plastics, resins, adhesives, paints, desiccants and flame retardants all pose a fairly significant risk of containing one or more SVHC.

Several of the SVHC on the Candidate List may be found in polymer containing parts of white appliances and consumer electronics. According to the results of many SVHC analysis and investigations the most rarely seen SVHCs in home appliances and consumer electronics sector are phthalate esters, especially DEHP, which are used in PVC parts as a plasticizer mostly in PVC cables.

For this reason, this study focused on phthalates included in the SVHC list. Products and materials may be tested for phthalates using analytical test methods. The identification and quantitation of phthalates requires an analytical technique which can separate each phthalate from other additives and from the plastic matrix itself. Gas chromatography/mass spectrometry (GC/MS) is an excellent instrumental platform for this analysis. The gas chromatograph separates analytes, while the mass spectrometer response is correlated to the amount of phthalate and will confirm the identification.

In this study, the REACH Regulation requirements were summarized for home appliances and consumer electronics manufacturers, the use applications of SVHCs were researched and the usage in polymeric materials were examined in detail. The most common SVHCs (phthalates) test methods were investigated and GC/MS analysis of phthalates done for some polymeric parts of a washing machine and the results were reported.

POLİMER İÇERİKLİ MALZEME ÜRETİMİNDE KULLANILAN BAZI KATKI MADDELERİNİN İNCELENMESİ

ÖZET

Çevremizde bulunan ve kullandığımız çoğu malzeme, polimer içermektedir. Polimerler çeşitli malzemelerin üretiminde kullanılabilir. Bu çalışma kapsamında yer alan beyaz eşya ve tüketici elektroniğinde kullanılan birçok parça içeriğinde polimerik malzemeler bulunmaktadır.

Polimerler gerekli fonksiyonel özellikler elde etmek için yardımcıları içermektedir. Yüksek kalitede ürünler elde etmek için bu yardımcıların her birinin optimum miktarlarda bulunması gerekmektedir. Bu yardımcıları katkı ve düzenleyicilerdir. Katkı maddeleri küçük miktarlarda düzenleyiciler ise büyük miktarlarda kullanılmaktadır. Katkı maddeleri polimerin mekanik özelliklerini etkilemezken, düzenleyiciler mekanik özellikleri değiştirmektedir. Katkı ve düzenleyiciler polimere polimerizasyondan sonra eklenmektedir. Bazen polimerin işlenmesine yardımcı olurken bazen de polimerlerin performans özelliklerini geliştirebilmektedirler. Plastikleştiriciler, antioksidanlar, ısı ve UV sabitleyiciler, alev geciktiriciler, renklendiriciler, dolgular başlıca polimer yardımcılarıdır. Kullanılan katkıların polimerle uyumlu ve karışabilir olması çok önemlidir ve bu katkının miktarını sınırlamaktadır. Katkı olmadan, polimerler teknik özellikler açısından kullanıma uygun değilken, katkıların kullanılması halinde plastikler daha güvenli, temiz, sağlam ve renkli özelliklerde olmaktadır.

BCC 2001 ve 2006 yılları raporlamasına göre, Avrupa Birliği'nde 2006 yılında 2.7 milyon ton plastik katkıları kullanılmıştır. Plastikleştiricilerin %56'lık kullanım oranıyla pazarda baskın bir payı bulunmaktadır. Alev geciktiriciler ise pazarda ikinci sırada yer almaktadır.

Plastikleştiriciler, polimerlerin esnekliğini, uzamasını ve işlenebilirliğini artıran katkılarıdır. Ftalat esterleri ise düşük fiyatları, kullanım kolaylığı ve elverişliliği sebebi ile en yaygın kullanılan plastikleştirici türleridir. Diğer yaygın plastikleştiriciler ise adipatlar, polimerik katkı ve trimelitatlardır.

Plastikleştiricilerin yüzde 90 oranından fazlası esnek PVC (polivinilklorür) uygulamalarında kullanılmaktadır. Plastikleştiriciler PVC'ye her oranda katılabilir. Bu nedenle plastikleştirilmiş PVC beyaz eşya ve tüketici elektroniği de dahil olmak üzere birçok çeşit üründe kullanılabilir.

REACH, kimyasalların kaydı, değerlendirilmesi, izni ve kısıtlanmasını öngören bir Avrupa Birliği mevzuatıdır. Avrupa Birliği (AB)'nde (Avrupa Ekonomik Alanında yer alan ülkeleri de kapsamaktadır) üretilen veya ithal edilen neredeyse tüm ürünleri kapsayan bir mevzuattır. Kırtan fazla yönetmelik ve tüzüğünü kapsayan, bunları tek bir şemsiye altında toplayan kompleks bir tüzüktür (Regulation (EC) No 1907/2006).

REACH'in bir kaç amacı vardır:

- Çevre ve insan sağlığını, kimyasal kullanımından yüksek düzeyde korumayı sağlamak.
- Kimyasalları piyasaya süren insanları (üretici ve ithalatçı / ihracatçı) kullanım amaçlarına ilişkin risklerin anlaşılması ve yönetiminden sorumlu tutmak.
- Maddelerin AB pazarında serbest hareketini sağlamak.
- AB kimya sanayiinde rekabetin ve yenilikçiliğin artırılması.
- Maddelerin zararlı özelliklerinin değerlendirilmesi için alternatif yöntemleri özendirme.

Kimi kimyasalların kansere neden olabilen (karsinojenik), genetik değişime yol açabilen (mutajenik), canlıların üremelerinde zehir etkili (reprotoksik), çevrede uzun sürede parçalanmayan (kalıcı kirletici), hayvanların dokularında birikim yapan (biyobirikimli) zararlı etkileri bulunmaktadır. Bunlar 'SVHC' (yüksek önem arz eden) maddelerdir. Bu kategori, canlılarda 'endokrin sistemi parçalayıcılar' gibi eşdeğer risk gösteren kimyasalları da kapsamaktadır.

Bu tür maddelerin eşyalar içinde kullanımı da kontrol edilmeye çalışılmaktadır. ECHA (Avrupa Kimyasallar Ajansı), bu tür kimyasalları bir 'Aday Liste' halinde yayımlamakta ve bu listeyi en azından iki yılda bir güncellemeyi amaçlamaktadır. Bu listedeki maddeler daha sonra izin prosedüründeki adımlardan geçerek, REACH Tüzüğü Ek XIV'e girecek ve 'İzne Tabi Maddeler' arasında yer alacaktır.

REACH' in amaçlarından biri de, izin prosedürü yoluyla bu tür kimyasalları denetim altında tutmak ve bunların daha güvenilir maddelerle değiştirilmesi için endüstriyi özendirme.

REACH, beyaz eşya ve tüketici elektroniği ürünlerinin tümünü de kapsamakta ve bu sebeple beyaz eşya ve tüketici elektroniği sektörünü güvenilir maddeler ve alternatif arayışları konusunda araştırmaya ve çalışmaya zorlamaktadır.

SVHC (yüksek önem arz eden maddeler) listesi, plastikleştiriciler, alev geciktiriciler, gibi polimer performans kimyasalları ve ve bilerek ya da geri dönüşüm kullanımı nedeniyle eklenen çeşitli fonksiyonel katkı maddelerini de içermektedir. Bu sebeple plastikler, kauçuklar, yapıştırıcılar, boyalar, kurutucular ve alev geciktiriciler SVHC içerme açısından yüksek risk taşıyan malzemeledir.

Aday listede bulunan bu SVHC maddelerinin beyaz eşya ve tüketici elektroniği ürünlerinin polimer içeren kısımlarında da bulunma ihtimali bulunmaktadır. Laboratuvarlar tarafından yapılan birçok SVHC analizi ve araştırmasına göre bu sektörde sıklıkla rastlanan SVHC maddeleri ftalat esterleridir, ftalatlardan ise en çok kullanılan DEHP (bis (2-etilhekzilftalat)) maddesidir. Bu maddeye PVC kısımlarda (özellikle PVC kablolarında) sıkça rastlanmaktadır.

Beyaz eşya ve tüketici elektroniği sektöründe en çok rastlanan SVHC maddesinin ftalat esterleri olması sebebi ile bu çalışmada SVHC listesinde bulunan ftalatlar üzerinde odaklanılmıştır. Ürün ve malzemelerin, analitik test metotları kullanılarak ftalat analizleri yapılabilmektedir. Ftalatların tanımlanması ve miktar tayininin yapılması için her bir ftalatı birbirinden ve polimer matrisin kendisinden ayıracak bir analitik metoda ihtiyaç duyulmaktadır. Bu analiz için gaz kromatografi/kütle spektrometresi (GC-MS) en uygun enstrümantal yöntemdir. Gaz kromatografisi analitleri ayırırken, kütle spektrometresi ftalat miktarı ile ilişkili ölçümü yapacak ve ftalat tanımlaması bu sayede gerçekleşecektir.

Bu alıřmada, beyaz eřya ve tüketiciler elektronik sektörü için REACH Tüzüğü yükümlülükleri özetlenmiş, SVHC kullanımı uygulamaları araştırılmış ve polimerik malzemelerdeki kullanım alanları detaylı olarak açıklanmıştır. Bu sektörde yaygın olarak rastlanan SVHC maddelerinden olan ftalatların analizi için test metotları araştırılmış ve amařır makinesinden seçilen altı eřit polimerik paradan örnekler hazırlanarak GC/MS metodu kullanılarak ftalat tayini yapılmış ve sonuçları raporlanmıştır.

1. INTRODUCTION (REACH - THE NEW EU CHEMICALS POLICY)

REACH is the Regulation for **R**egistration, **E**valuation, **A**uthorisation and **R**estriction of **C**hemicals. It entered into force on 1st June 2007 to streamline and improve the former legislative framework on chemicals of the European Union (EU). REACH places greater responsibility on industry to manage the risks that chemicals may pose to the health and the environment [1].

REACH has several aims:

- To provide a high level of protection of human health and the environment from the use of chemicals.
- To make the people responsible who place chemicals on the market (manufacturers and importers responsible for understanding and managing the risks associated with their use.)
- To allow the free movement of substances on the EU market.
- To enhance innovation in and the competitiveness of the EU chemicals industry.
- To promote the use of alternative methods for the assessment of the hazardous properties of substances e.g. quantitative structure-activity relationships (QSAR) and read across [2].

The regulation sets out new requirements for chemicals and substances manufactured within or imported into the EU to ensure that substances (including refinery streams and substances used to produce them in the EU) can continue to be used. Each substance, along with every identified use, will need to be registered with the European Chemicals Agency (ECHA) [3].

REACH is based on the idea that industry itself is best placed to ensure that the chemicals it manufactures and puts on the market in the EU do not adversely affect human health or the environment. This requires that industry has certain knowledge of the properties of its substances and manages potential risks [4].

REACH is the most comprehensive chemicals legislation in the world, and is also likely to become one of the most complicated to comply with—at all levels from the technical to managerial and business challenges. It will also have global implications. Even those not immediately involved in the EU market are in the supply chain of others who are, and will be asked for information and support by those formulators who do, or whose customers decide not to, support substances that are currently exported to the EU [3].

To comply with REACH Regulation, one of the most complex requirement for home appliances and consumer electronics manufacturers is the Substances of Very High Concern (SVHC) List. Several of the SVHC on the Candidate List may be found in polymer containing parts of white appliances and consumer electronics. According to the results of many SVHC analysis and investigations the most rarely seen SVHCs in home appliances and consumer electronics sector are phthalate esters, especially DEHP (bis (2-ethylhexyl) phthalate), which are used in PVC (poly (vinyl chloride)) parts as a plasticizer mostly in PVC cables and the other common substances are flame retardants HBCDD (hexabromocyclododecane) used in PS (polystyrene) materials.

In this study, the REACH Regulation requirements were summarized for home appliances and consumer electronics manufacturers, the use applications of SVHCs were researched and the usage in polymeric materials were examined in detail. Finally analysis methods of the most common SVHCs (phthalates) were investigated for complying with REACH and done for some polymeric parts of a washing machine and the results were reported.

2. THEORY

2.1 REACH Steps

2.1.1 Registration

REACH requires all chemicals manufactured in or imported into the EU in a volume of 1 tonne or more per year to be registered with the competent authority within a new European Chemicals Agency (ECHA). Registration means that a manufacturer or importer has provided a registration dossier to the Agency and not received any indication that it is incomplete. This does not by itself mean that the dossier is in compliance with the legislation nor does it mean all the properties of the registered substance have been identified [4].

The ECHA will manage a central, EU-wide database. Companies will have to submit basic information including a brief description of the uses of the substance and any uses that the manufacturer advises against, a technical dossier of test data and future testing proposals. Data requirements vary according to the production volume and suspected toxicity of the substance. Registration will be undertaken in several stages, with deadlines varying with production volumes (Figure 2.1) [5].

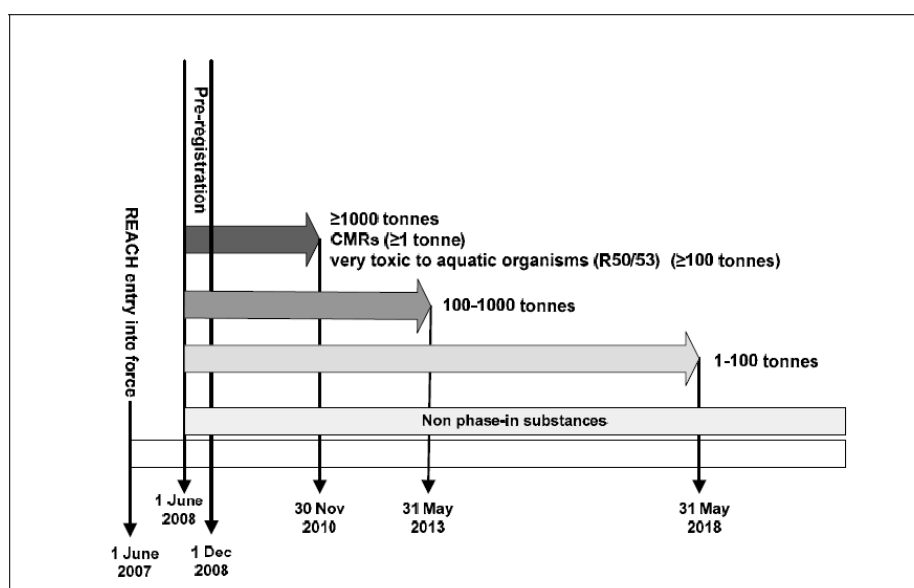


Figure 2.1 : Registration deadlines.

Failure to register means that the substance cannot be exported.

Registrant need to submit those information about substances for the registration purposes:

- Substance identity
- Physicochemical properties
- Mammalian toxicity
- Ecotoxicity
- Environmental fate, including abiotic and biotic degradation
- Information on manufacture and use(s) as well as risk management measures

Regardless of tonnage, the registrant must always provide all relevant physicochemical, toxicological and ecotoxicological information that is available to him even if not required (e.g. information he holds himself or that he can obtain from other information sources) [6].

The only actors in the supply chain with registration obligations are:

- EU manufacturers and importers of substances on their own or in mixtures.
- EU producers and importers of articles meeting the criteria explained in the Guidance for articles.
- “Only representatives” established in the EU and appointed by a manufacturer, formulator or article producer established outside the EU to fulfil the registration obligations of importers.

Although polymers are exempted from registration, manufacturers or importers of polymers have, in certain circumstances, registration obligations.

Registration of substances imported into the EU on their own, in mixtures or in articles will have to be submitted by the EU importers. This implies that each individual importer needs to register the substance(s) he imports. Natural or legal persons that manufacture substances, formulate mixtures or produce articles outside the EU cannot themselves register a substance(s). However, they can appoint an only representative established within the EU to carry out the required registration of the substance that is imported into the EU (*REACH Article 8(1)*). This will relieve the

EU importers within the same supply chain from their registration obligations, as they will be regarded as downstream users [7].

2.1.2 Evaluation

The Agency and the Member States Competent Authorities will carry out different types of evaluations to determine the need for further information on the registered substance.

There are three types of evaluation, covering three different objectives:

- Dossier evaluation: The Agency will perform the following checks of the registration dossiers:
 - Compliance check: The Agency may select any registration dossier to check whether the appropriate information is available and has been adequately reported. The registrant may be asked to submit further information if necessary.
 - Checking of testing proposals: for chemicals manufactured or imported in a quantity of 100 tonnes or more, no testing shall be conducted for the information specified in Annexes IX and X of the REACH Regulation. Instead a testing proposal must be submitted in the registration dossier. The Agency shall then evaluate whether the testing proposal is adequate before such a test is performed. The objective of this procedure is to prevent unnecessary animal testing, i.e. the repetition of existing tests, and poor quality tests.
- Substance evaluation: When the Agency or a Member State Competent Authority has an indication that a substance may pose a risk to human health or the environment, the Agency will include that substance on a list for “substance evaluation”. For each substance on this list, one Member State shall evaluate in more detail whether further information is needed and in that case the registrant(s) will be requested to provide such information.

Substance evaluation may lead to conclusions such as:

- action needs to be taken under the restriction or authorisation procedures
- classification and labelling needs harmonising under REACH

- information needs to be given to other authorities to take appropriate action under other legislation [8].

2.1.3 Authorization

Substances identified through registration and/or evaluation as being of high concern will be subject to authorisation. Without authorisation, these substances cannot be used or placed on the market. Authorisation will be granted (one for each use and user) if the risks associated with a substance can be proved by industry to be “adequately controlled”. It may also be granted if the socio-economic benefits of continued use are considered to outweigh the risks. This type of decision may take into account whether industry is actively researching to find an alternative substitute. Authorisations granted for socio-economic reasons will be time-limited and reviewed on a case-by-case basis. The use of other substances that pose unacceptable risks, but are not classified as of high concern, could be restricted if requested by a member state. Restriction may ban use in certain products, by consumers, or even any use at all [5].

Authorization steps are:

Step 1 - Identification of substances of very high concern: Substances of very high concern can be identified on the basis of the criteria:

- Carcinogenic, Mutagenic or toxic to Reproduction (CMR) classified in category 1 or 2,
- Persistent, Bioaccumulative and Toxic (PBT) or very Persistent and very Bioaccumulative (vPvB) according to the criteria in Annex XIII of the REACH Regulation, and/or
- identified, on a case-by-case basis, from scientific evidence as causing probable serious effects to humans or the environment of an equivalent level of concern as those above e.g. endocrine disrupters.

This will be done by Member State Competent Authorities or the Agency (on behalf of the European Commission) by preparing a dossier in accordance with Annex XV. Interested parties can comment on substances for which a dossier has been prepared. The outcome of this identification process is a list of identified substances, which are candidates for prioritisation (the “candidate list”).

Step 2 - Prioritisation process (by authorities): The substances on the candidate list are then prioritised to determine which ones should be subject to authorisation. Interested parties are invited to submit comments during this process. At the end of the prioritization process, the following decisions are taken:

- whether or not the substance will be subject to authorisation;
- which uses of the included substances will not need authorisation (e.g. because sufficient controls established by other legislation are already in place);
- the “sunset date” by when a substance can no more be used without authorisation.

Step 3 - Applications for authorization (by industry): Applications for authorisation need to be made within the set deadlines for each use that is not exempted from the authorisation requirement. They must include among others:

- a chemical safety report covering risks related to those properties that caused the substance to be included in authorisation system (unless already submitted as part of the registration)
- an analysis of possible alternative substances or technologies including, where appropriate, information on research and development foreseen or already in progress to develop such alternatives.

If the analysis of alternatives reveals that there is a suitable alternative, the applicant must submit a substitution plan, explaining how he intends to replace the substance by the alternative. The suitability of available alternatives is assessed taking into account all relevant aspects, including whether the alternative results in reduction of overall risks and is technically and economically feasible.

An applicant can include a socio-economic analysis in his application, but in cases where he is not able to demonstrate adequate control of risks and where no suitable alternative exists, he needs to include one in his application.

A fee has to be paid for each application.

For all applications, the Agency will provide expert opinions. The applicant can comment on these opinions.

Step 4 - Granting of authorizations (by the European Commission): Authorisations will be granted if the applicant can demonstrate that the risk from the use of the substance is adequately controlled. The “adequate control route” does not apply for substances for which it is not possible to determine thresholds and substances with PBT or vPvB properties.

If the risk is not adequately controlled, an authorisation may still be granted if it is proven that the socio-economic benefits outweigh the risks and there are no suitable alternative substances or technologies.

Downstream users may only use such substances for uses which have been authorised.

For this they must either:

- obtain the substance from a company that was granted an authorisation for that use. They must stay within the conditions of that authorisation. Such downstream users must notify the Agency that they are using an authorised substance.
- apply themselves for authorisations for their own uses [9].

European Commission announced on 17th February 2011 that the first set of six substances (see Table 2.1) subject to authorisation under REACH has been officially added to Annex XIV, or the authorisation list, of the Regulation [10].

2.1.4 Restriction

REACH foresees a restriction process to regulate the manufacture, placing on the market or use of certain substances within the EU territory if they pose an unacceptable risk to health or the environment. Such activities may be limited or even banned, if necessary. The restriction is designed as a “safety net” to manage risks that are not addressed by the other REACH processes.

Any substance on its own, in a preparation or in an article may be subject to restrictions if it is demonstrated that risks need to be addressed on a Community-wide basis.

Restrictions of a substance can apply to all uses or to specific uses.

Table 2. 1 : First six authorized substances.

| Nr | Substance | Intrinsic propertyies referred to in Article 57 | Latest application date | Sunset date |
|-----------|--|--|--------------------------------|--------------------|
| 1 | 5-tert-butyl-2,4,6- trinitro-m-xylene (Musk xylene) EC No: 201-329-4 CAS No: 81-15-2 | vPvB | 21 February 2013 | 21 August 2014 |
| 2 | 4,4'- Diaminodiphenylmethane (MDA) EC No: 202-974-4 CAS No: 101-77-9 | Carcinogeni c | 21 February 2013 | 21 August 2014 |
| 3 | Hexabromocyclododecane (HBCDD) EC No: 221-695-9, 247-148-4, CAS No: 3194-55-6 25637-99-4 alpha-hexabromocyclododecane CAS No: 134237-50-6, beta-hexabromocyclododecane CAS No: 134237-51-7 gamma-hexabromocyclododecane CAS No: 134237-52-8 | PBT | 21 February 2014 | 21 August 2015 |
| 4 | Bis(2-ethylhexyl) phthalate (DEHP) EC No: 204-211-0 CAS No: 117-81-7 | Toxic for reproductio n | 21 August 2013 | 21 February 2015 |
| 5 | Benzyl butyl phthalate (BBP) EC No: 201-622-7 CAS No: 85-68-7 | Toxic for reproductio n | 21 August 2013 | 21 February 2015 |
| 6 | Dibutyl phthalate (DBP) EC No: 201-557-4 CAS No: 84-74-2 | Toxic for reproductio n | 21 August 2013 | 21 February 2015 |

There is no tonnage threshold for a substance to be subject to restriction.

Annex XVII of the REACH Regulation contains the list of all restricted substances, specifying which uses are restricted. The existing restrictions set out in the Marketing and Use Directive (76/769/EEC), e.g. the ban on asbestos and restrictions on the uses of certain azo-dyes, were carried over to REACH [11].

2.2 Obligations of White Appliances and Consumer Electronics Sector Under REACH

"Article means an object which during production is given a specific shape, surface or design which determines its function to a greater degree than does its chemical composition. (REACH Regulation Article 3.3)" [12].

Most of the commonly used objects in private households and industries are articles, e.g. furniture, clothes, vehicles, books, toys, kitchen equipment, and electronic equipment. It may be very simple, like a wooden chair but could also be rather complex, like a computer, consisting of several parts, which are also considered articles [13].

A White Appliances and Consumer Electronics Company has the role of an article producer, if it produces articles within the EU, regardless of how it is produced and where the article is placed on the market. An article importer is any company located inside the EU which imports articles from countries which are located outside the EU. An article supplier is a company which produces, imports or distributes articles and/or places them on the EU market. Retailers are also article suppliers. Non-EU producers of articles may appoint "Only Representatives" to fulfil all obligations of the importers of their articles into the EU.

Four types of requirements exist for A White Appliances and Consumer Electronics Company as a producer, importers or suppliers of articles: to register (1) or notify (2) substances contained in articles to the Chemicals Agency, to communicate specific information related to the content of some specific substances to the customers (3) and to comply with any community wide restriction (4). These obligations only apply under certain conditions, which are specified in Article 7, 33 and the entries in Annex XVII of REACH. Article suppliers, which are only supplying (i.e. not themselves producing or importing the articles), only have to comply with Article 33 [14].

2.2.1 Registration according to Article 7(1)

A registration (Article 7.1) of substances in articles is obligatory for an article producer or importer only if the following conditions are met:

"7(1) Any producer or importer of articles shall submit a registration to the Agency for any substance contained in those articles, if both the following conditions are met:

(a) the substance is present in those articles in quantities totalling over one tonne per producer or importer per year;

(b) the substance is intended to be released under normal or reasonably foreseeable conditions of use"[12]

Even if the above criteria are met for a substance in an article, the substance does not have to be registered by the article producer or importer if it has already been registered for that use (Article 7(6)).

Hence, in order to identify a possible obligation to register a substance in articles it needs to be checked if the 1 tonne per year threshold is exceeded. For this the identity and the tonnage of the actual substance do not always have to be known, as the 1 tonne per year threshold can initially be compared to:

1. the total tonnage of all articles with intended release produced and/or imported, and to

2. the total tonnage of all substances and mixtures intended to be released incorporated in these articles.

When calculating the tonnage of a substance intended to be released contained in articles, the following points should be taken into account:

- Not only the amounts intended to be released but the total amount in the articles needs to be considered. Thus, if the substance is also part of the article matrix, these amounts have to be considered as well.
- Only the amount of the substance that is actually in the final articles has to be considered, i.e. any amount that is incorporated in the articles and then lost during further production steps (e.g. through evaporation or wash out) does not have to be considered.
- If the same substance is intended to be released from different articles of one
- producer/importer, the substance volumes in all those articles have to be summed up.

Guidance on how to prepare a registration dossier is provided in the Guidance on registration which is published by ECHA.

A release of substances from articles is intended if it fulfils an accessory function which is deliberately planned and would not be achieved if the substance were not released. In the case of scented articles, for example, the fragrance substances need to be released in order for the article to be smelled. Consequently, substances that are released because of ageing of articles, because of wear and tear or as an unavoidable side-effect of the functioning of the article, are generally not intended releases, as the release as such does not provide a function in itself.

If the release of a substance from an object fulfils the main function of the object the release is not regarded as “intended release” for the purpose of REACH. In this case the object usually would be considered as a combination of an article (functioning as a container or a carrier material) and a substance/mixture, and not as an article with intended release of a substance/mixture [14].

Examples for intended releases:

- releases from a scented eraser: An eraser (rubber eraser) consists of an elastic material (rubber or resin components) and additive agents such as fillers and polishing materials. Fragrance substances can also be added to provide an accessory function of a good smell. The fragrance substances only fulfil their function if they can be inhaled and thus it is intended that they are released [13].
- silver ion washing machines: Samsung Electronics’ silver ion washing machines use electrolysis to generate silver ions which are released in very small quantities during the wash cycle. This constitutes an intentional release [15].

An intended release of a substance from an article has furthermore to occur under (normal or reasonably foreseeable) conditions of use. This means that the substance release has to occur during the service life of the article. Hence, a substance release during the production or disposal phase of the article’s life cycle is not an intended release [14].

A release is not considered to be an intended release in the following cases:

- A release occurs during removal of 'impurities' from a semi-finished or finished article during its production process (before marketing as a finished article).
- A release occurs during use or maintenance of the article and is meant to improve the product quality in a wide sense or the safety as a side effect but the released substances do not contribute to the function of the article.
- A release of substances is an unavoidable side-effect of the functioning of the article. Without the release, the article would not work, but the release is not directly intended.
- A release of substances formed during chemical reactions of any kind.
- A release is incidental, could be forced by undue use or in an accident [13]

2.2.2 Notification according to Article 7(2)

The article 7(2) of REACH Regulation imply that:

"7(2) Any producer or importer of articles shall notify the Agency, in accordance with paragraph 4 of this Article, if a substance meets the criteria in Article 57 and is identified in accordance with Article 59(1), if both the following conditions are met:

(a) the substance is present in those articles in quantities totalling over one tonne per producer or importer per year;

(b) the substance is present in those articles above a concentration of 0.1 % weight by weight (w/w)."[12]

So notification of substances in articles is required of producers and importers of articles when all conditions of Article 7(2) are met:

- The substance is included in the Candidate List for authorisation.
- The substance is present in articles produced and/or imported above a concentration of 0.1% (w/w).
- The total amount of the substance present in all articles produced and/or imported, which contain more than 0.1% (w/w) of the substance, exceeds 1 tonne per actor per year.

If, however, one or both of the following conditions are met, no notification is required:

- The producer or importer can exclude exposure of the substances to humans or the environment during normal or reasonable foreseeable conditions of use including disposal (Article 7(3)).
- The substance has already been registered for that use according to Article 7(6).

The substance concentration threshold of 0.1% (w/w) applies to the article as produced or imported. In practice, however, companies may already be collecting information not only on the whole article but also on parts thereof. Companies may, on a voluntary basis, prepare their notification to ECHA on this basis.

The obligation to notify substances in articles also applies to packaging materials, which may be produced or imported separately as packaging of imported goods. Packaging is to be assessed separately from any object it contains.

A notification of substances in articles shall be made at the latest 6 months after it has been included on the Candidate List of Substances of Very High Concern for authorisation, but only starting from 1 June 2011. This means that for substances included in the Candidate List before 1 December 2010, the notifications have to be submitted not later than 1 June 2011. For substances included in the Candidate List on or after 1 December 2010, the notifications have to be submitted no later than 6 months after the inclusion.

The information to be notified according to Article 7(2) shall include the following items:

- the identity and contact details of the producer or importer of the articles
- the registration number for the substance, if available
- the identity of the SVHC (this information is available from the Candidate List and the supporting documentation)
- the classification of the substance (this information is available from the Candidate List and the supporting documentation)
- a brief description of the use(s) of the substance in the article(s) as specified in section 3.5 of Annex VI and of the uses of the article(s)
- the tonnage range of the substance contained in the articles, i.e. 1-10 tonnes, 10-100 tonnes, 100-1000 tonnes or ≥ 1000 tonnes.

2.2.3 Obligations according to Article 33

The Article 33 of REACH Regulation imply that:

"33(1). Any supplier of an article containing a substance meeting the criteria in Article 57 and identified in accordance with Article 59(1) in a concentration above 0,1 % weight by weight (w/w) shall provide the recipient of the article with sufficient information, available to the supplier, to allow safe use of the article including, as a minimum, the name of that substance.

33(2). On request by a consumer any supplier of an article containing a substance meeting the criteria in Article 57 and identified in accordance with Article 59(1) in a concentration above 0.1 % weight by weight (w/w) shall provide the consumer with sufficient information, available to the supplier, to allow safe use of the article including, as a minimum, the name of that substance.

The relevant information shall be provided, free of charge, within 45 days of receipt of the request."[12].

The aim of Article 33 is to ensure that sufficient information is communicated down the supply chain to allow the safe use of articles.

A supplier of articles containing a SVHC included on the Candidate List for authorisation in a concentration above 0.1% (w/w) has to provide relevant safety information about this substance available to him to the recipients of these articles. If no particular information is necessary to allow safe use of the article containing a substance from the Candidate List, as a minimum the name of the substance in question has to be communicated to the recipients. The information is to be provided to the recipients automatically, i.e. as soon as the substance has been included on the Candidate List for authorisation. Note that the term "recipients" refers to industrial or professional users and distributors, but not to consumers.

Upon request of a consumer, the same supplier of articles has to provide relevant safety information about the SVHC available to him also to this consumer. If no particular information is necessary to allow safe use of the article, as a minimum the name of the substance in question has to be communicated to the consumer. The consumer has to be provided with this information within 45 calendar days of the request and free of charge.

When determining the SVHC concentration in articles, a SVHC on the Candidate List may be contained in different concentrations in different components of the same article, e.g. one concentration in the chassis of a laptop and another concentration in the transformer. For obligations according to Article 7(2) and 33 to apply, the concentration of this SVHC has to exceed 0.1% (w/w) in the entire article. In order to check this condition firstly it needs to be known for each component whether it contains above 0.1% (w/w) of the SVHC or not.

To illustrate the cases that may arise when checking the 0.1% threshold, the example of the laptop assembled from different components, such as transformer, motherboard, memory, processor, chassis, etc. is taken up:

If no component contains above 0.1% (w/w) of a SVHC on the Candidate List, also the entire laptop does not contain above 0.1% (w/w).

If one or more components contain above 0.1% (w/w) of a SVHC on the Candidate List, the producer/importer of laptops needs to:

1. find out the concentration of the SVHC in each component and the mass of each component containing the SVHC (whether above 0.1% (w/w) or below),
2. calculate the mass of the SVHC in each of these components
3. calculate the average concentration of the SVHC in the laptop using the formula below and check if it is above 0.1% (w/w).

Likewise, if a producer of laptops adds himself a SVHC to one or more parts of the laptop, he has to follow the same approach in order to check whether the 0.1% threshold is exceeded for the laptop he finally places on the market.

As concerns the obligations to communicate information on substances in articles in general (i.e. communication with recipients and consumers), please note that:

- There is no tonnage trigger for these obligations (i.e. they also apply below 1 tonne per year).
- Packaging is always to be treated as article(s) separate from the contents of the packaging. Therefore, the obligations to communicate information on substances in articles also apply to packaging materials.
- The substance concentration threshold of 0.1% (w/w) applies to the article as supplied. In practice, however, companies may already be collecting

information not only on the whole article but also on parts thereof. Companies may, on a voluntary basis, follow this approach when communicating in accordance with Article 33.

- The obligations also apply to articles which were produced or imported before the substance was included in the Candidate List and are supplied after the inclusion. Thus, the date of supply of the article is the relevant date.
- The substance name to be communicated is the one appearing on the Candidate List for authorisation.

REACH does not specify a format for providing information with articles. You must choose a format that will ensure that the recipient can readily become aware of the information [14].

2.2.4 Restrictions according to Article 67

REACH foresees a restriction process to regulate the manufacture, placing on the market or use of certain substances within the EU territory if they pose an unacceptable risk to health or the environment. Such activities may be limited or even banned, if necessary. The restriction is designed as a “safety net” to manage risks that are not addressed by the other REACH processes.

The Restriction List consist of substance names as well as the condition of restriction. A substance may be limited or banned for a use in an article, so the article suppliers too need to check the Restriction List which is recently updated under REACH [13].

2.3 Substances of Very High Concern (SVHC)

2.3.1 Why regulate chemicals?

Chemicals produced by humans form the strands of a complex societal web. The network begins with the production of a single chemical that branches out into hundreds of uses. Several hundred chemicals can be used or created in the process of producing one final product.

Whether natural or man-made, a chemical has the potential of causing harm to a living organism. Water can present a risk of drowning to a bathing human. Iron can be fatal to humans or animals when ingested in very high quantities, yet it is an essential mineral for the functioning of most organisms. Similarly, negative effects of

a given chemical depend on complex biochemical interactions. For instance, chromium acts as a potent carcinogen and skin sensitiser in a fully oxidised state, but its reduced trivalent state exhibits few signs of having a toxic mechanism in organisms.

The term ‘hazard’ describes the intrinsic physical and toxicological properties of a chemical. ‘Risk’ relates to the possibility and severity of damage to humans or ecosystems after exposure to a chemical. Defining risk levels must also account for the perceived nature of danger, as well as the potential benefits of a risky activity. Regulating chemicals responds to the need to control existing or potential risks, while retaining the socioeconomic benefits arising from the production and use of chemicals [16].

These substances have hazardous properties of such high concern that it is essential to regulate them centrally through a mechanism that ensures that the risks related to their actual uses are assessed, considered and then decided upon by the Community. This is justified because the effects on humans and the environment of these substances are very serious and normally irreversible. Substances that fall into these categories will be fed into the authorisation system as resources allow [4].

2.3.2 What are chemicals?

Whether naturally-occurring or synthetic, the term ‘chemical’ refers to substances and preparations. The former are elements and their compounds, whereas preparations are mixtures and solutions of substances. ‘Chemical products’ does include ‘articles’ which are manufactured products or materials with specific form (e.g., plastics). The European Commission proposes that an article should be defined as ‘an object composed of substance(s) and/or preparation(s) which during production is given a specific shape, surface or design determining its end use function to a greater degree than its chemical composition does’.

Substances and preparations may be present within articles (e.g., ink in a pen) where the article services as a container or chemical delivery device. Substances and preparations can provide a material matrix or form an integral part of an object, where only minute quantities of a chemical may be released (such as a dyed textile). It is therefore important to understand that during manufacture, substances and preparations can be bound within the matrix of an article (e.g., pigment in a plastic)

or onto the surface of a matrix (e.g., layer of paint on a plastic). Various mechanisms of binding are available, depending on the process and the chemicals/materials used.

Chemical products available on the market can be categorised according to their function and use. Because a single chemical can have hundreds of uses, the details of specific uses become a major factor when determining the appropriateness of a risk management option. Every industry sector makes some use of chemicals, from electrical engineering to publishing as seen on Figure 2.2.

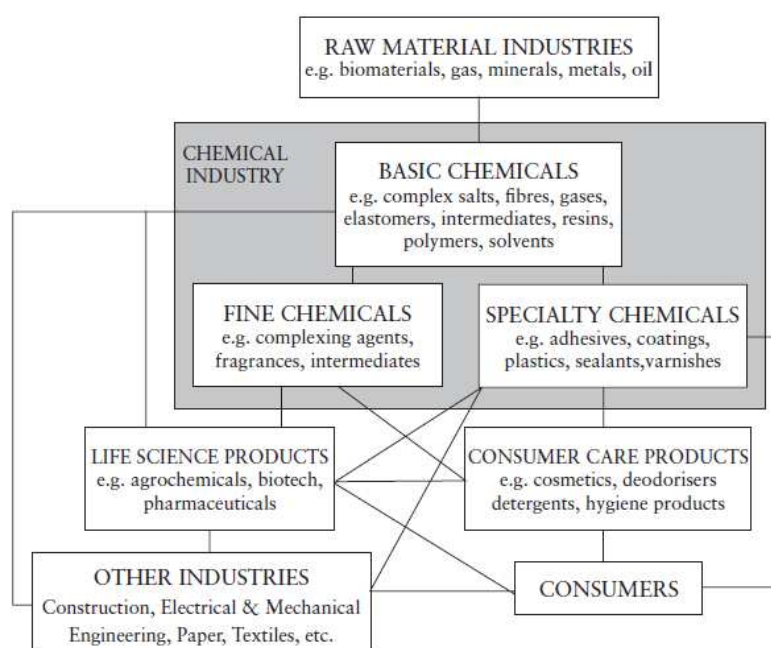


Figure 2.2 : Chemical industry classification.

In principle REACH applies to all chemicals: not only chemicals used in industrial processes but also in our day-to-day life, for example in cleaning products, paints as well as in articles such as clothes, furniture and electrical appliances [16].

Some substances are specifically excluded:

- Radioactive substances
- Substances under customs supervision
- The transport of substances
- Non-isolated intermediates
- Waste
- Some naturally occurring low-hazard substances

Some substances, covered by more specific legislation, have tailored provisions, including:

- Human and veterinary medicines
- Food and foodstuff additives
- Plant protection products and biocides

Other substances have tailored provisions within the REACH legislation, as long they are used in specified conditions:

- Isolated intermediates
- Substances used for research and development [2]

2.3.1 What is SVHC?

The following substances are considered substances of very high concern:

Substances meeting the criteria for classification in accordance with Directive 67/548/EEC:

- Carcinogenic category 1 or 2
- Mutagenic category 1 or 2
- Toxic for reproduction category 1 or 2
- Substances which are persistent, bioaccumulative and toxic (PBT) or very persistent and very bioaccumulative (vPvB) in accordance with the criteria set out in Annex XIII of REACH
- Substances having endocrine disrupting properties or substances having persistent, bioaccumulative and toxic properties or very persistent and very bioaccumulative properties or any other property giving rise to an equivalent level of concern to those substances listed above.

2.3.2 SVHC List

SVHCs List is a list of substances for authorisation for some or all uses. Updated list on 19th December 2011 is (included 6 authorized substances) shown in (listed with regard to ECHA's web page order) ANNEX A [17].

2.3.3 Potential usages of SVHCs

The following is an overview of the current SVHCs (updated 19th December 2011) and their possible uses:

Zirconia Aluminosilicate Refractory Ceramic Fibres and Aluminosilicate Refractory Ceramic Fibres (Annex VI, part 3, table 3.2 of Regulation (EC) No 1272/2008) are used for high-temperature insulation, almost exclusively in industrial applications (insulation of industrial furnaces and equipment, equipment for the automotive and aircraft/aerospace industry) and in fire protection (buildings and industrial process equipment) RCF may be used in electrical and domestic appliances, like glass ceramic hobs, electric ovens, electric grills, microwave ovens, in gas-fired apparatus or other devices with “open” flames and in kilns (for enamels, ceramics, or clay) for leisure and hobby use [18].

Calcium arsenate is used as a precipitating agent in copper smelting and manufacturing of diarsenic trioxide (As_2O_3) [19].

Bis(2-methoxyethyl) ether is used in the production of magnetic polystyrene beads and the manufacture of rubber and plastic products. Due to existing restrictions the use of the substance as such or in mixtures by consumers is not expected. In general consumer exposure to articles containing adhesives, paints, coatings etc. is theoretically still possible, as those articles are not restricted [20].

Potassium hydroxyoctaoxodizincatedichromate is used by five industrial activity sectors:

- formulation of coatings and sealants,
- industrial use of coatings in the aeronautic/aerospace sector,
- industrial use of coatings in the vehicle coating sector,
- industrial use of sealants,
- laboratory uses (analysis, R&D, etc.) in very small quantities, no more developed hereafter.

The largest chromates amount used is for paint production mainly as corrosion inhibitor and as pigments [21].

Lead dipicrate is an explosive like lead diazide and lead styphnate. It may be used in low amounts in detonator mixtures together with the two other mentioned lead compounds [22].

N,N-dimethylacetamide (DMAC) is used in following applications:

- Process solvent and reagent in the production of agrochemicals, pharmaceuticals and fine chemicals;

- Process solvent for spinning of fibres of various polymers including acrylic, polyurethane-polyurea copolymer (Elastane, Spandex) and poly(m-phenylene isophthalamide) (PMIA, meta-aramid);
- Process solvent in the production of polyimide and polysulphone films;
- Solvent in coatings e.g. polyamide-imide (PAI) enamels (varnishes) used for electrical wire insulation;
- Solvent in paint strippers (paint removers) and ink removers;
- Excipient (carrier ingredient) in human and veterinary pharmaceuticals;
- Laboratory uses.

For some of the uses as solvent, the DMAC will be present as a residue in polymers (e.g. textile fibres) and significant amounts of the substance is released by downstream uses of the polymers.

The major use of DMAC is as a process chemical in the production of pharmaceuticals, agrochemicals and fine chemicals [23].

Arsenic acid is used in following applications:

- Use as fining agent in the manufacture of speciality glass;
- Use in the production of copper foil for printed circuit boards.

Manufacture of ceramic glass is the principal application area for arsenic acid. The ceramic glass is mainly used for vitro-ceramic (glass-ceramic) plates for cookware and other high-temperature domestic appliances. But application of arsenic acid in the glass melt, the arsenic substances are transferred to a non-crystalline or vitreous inorganic macromolecular structure. Consequently arsenic acid would not be present in the final articles.

It must be expected that arsenic is present in imported printed circuit boards in electronic equipment, and also is present in imported printed circuit boards for manufacturing of electronic equipment [24].

2-Methoxyaniline; o-Anisidine is used for manufacture of azo, naphthol pigments and dyes and as a processing aid. These were mainly used in printing inks for packing materials like paper, cardboard, polymer and aluminum foil [25].

Trilead diarsenate be considered an intermediate in the production of diarsenic trioxide. Because of this reason trilead diarsenate is not used by downstream users or present in any consumer products [26].

1,2-dichloroethane is used as an intermediate in the synthesis of vinyl chloride monomer. However, the substance is also used as an intermediate in fine chemical synthesis and as a solvent in chemical and pharmaceutical industries [27].

Pentazinc chromate octahydroxide is used by four industrial activity sectors:

- formulation of liquid mixtures (coatings such as primer paints and wash primers, thinners, paint removers , etc.),
- industrial use of mixtures in the aeronautic/aerospace sector,
- industrial use of mixtures in the vehicle coating sector,
- laboratory uses (analysis, R&D, etc.) in very small quantities, no more developed hereafter.

Some doubtful uses of pentazinc chromate octahydroxide are also reported in the literature, for which no information is available:

- formulation of coating powders that are mixtures of pigments, resins, curing agents and other additives; they give durable finish and are used to coat metal window frames, many car components and most “white goods” such as fridge freezers and washing machines. Coating powders are sprayed by an electrostatic process that gives a fairly uniform thickness of coating,
- coloring and hiding power because of its structure and its tinting strength,
- anti-scaling agent, that may be related to the anti-corrosive function,
- plastic formulation and fireworks [28]

Formaldehyde, oligomeric reaction products with aniline (technical MDA) is used as a precursor to methylene diphenyldiisocyanate (MDI) mostly. Other uses of PMDA are:

- as a hardener for epoxy resins in
 - adhesives,
 - production of rolls with composite cover,
 - production of chemically resistant pipes
 - production of moulds,
- in the production of high performance polymers and
- as a starting point for the synthesis of 4,4'-methylenebis(cyclohexaneamine) (PACM) [29].

Bis(2-methoxyethyl) phthalate is used as a plasticiser in the production of nitrocellulose, acetyl cellulose, polyvinyl acetate, polyvinyl chloride and polyvinylidene chloride intended for contact with food or drink. DMEP is giving these polymeric materials good lightresistance. Further, it is used as a solvent. DMEP can improve the durability and toughness of cellulose acetate (e.g. in laminated documents) and can be used in enamelled wire, film, high-strength varnish and adhesive. It can also be used in pesticide products internationally [30].

4-(1,1,3,3-tetramethylbutyl)phenol is mainly used as an intermediate for the production of phenolic resins. Other uses are:

- As a monomer for polymer preparations
- As an intermediate for manufacture of ethoxylates which to some extent will be a component of products (e.g. paints) used by industry, professional users and consumers
- As a component in phenolic resins used in the formulation of adhesives which are used by industry, professional users and consumers.
- As a component in coatings, printing inks and some sorts of paints, which are used by industry, professional users and consumers
- As tackifier in the production of rubber products [31].

Lead diazide, Lead azide is used:

- as an initiator or booster in detonators used for both civilian and military uses; and
- as an initiator in pyrotechnic devices used in military munitions (fuzes) and space shuttles/satellites.

Another application likely to be relevant but unconfirmed is as a primer in cartridge actuated devices for aerospace/defence/safety applications [32].

Phenolphthalein uses can be divided into the following four categories:

- Preparation of mixtures (formulation): The preparation of mixtures containing phenolphthalein is carried out by chemical formulating companies.
- Laboratory use: Phenolphthalein is used as a chemical reagent in laboratories. Specifically, it is used as a pH indicator in solution for determining acid/alkali conditions via titration methods in chemical analysis.

- Use in other specialist applications:
 - Use in disappearing or colour-changing inks or dyes. The dye changes colour in the presence of an acid or a base.
 - Use in laboratory indicator test paper.
- Formulation of pharmaceutical preparations [33].

Dichromium tris(chromate) is used in:

- formulation of metal treatment products;
- industrial surface treatment of metals- reactive anti-corrosion primer for steel and aluminium;
- laboratory reagent (minor use).

Because of its corrosion inhibitor property, dichromium tris(chromate) is used in mixtures for specific uses such as chemical conversion against corrosion, post-treatment in hot dip galvanizing, pretreatment of organic coating, passivation (of galvanized steel sheets for instance).

Examples of sectors of use for such industrial surface treatment are construction and aeronautics [34].

Lead styphnate identified uses include:

- as an initiator in primers for percussion caps for small calibre and rifle ammunition;
- as an initiator in detonators for civilian and military use;
- in pyrotechnic igniters used in military munitions (fuzes);
- as a primer in cartridge actuated devices both for aerospace/defence/safety applications but also for cartridges used in fastening power tools; and
- as an initiator in pyrotechnics including automotive airbag inflators and seat belt pretensioners
- as a primer in cattle killer cartridges [35].

2,2'-dichloro-4,4'-methylenedianiline (MOCA) is used primarily to produce polyurethane articles. Polyurethanes are produced by the reaction of a liquid isocyanate with a blend of liquid polyols, catalysts and other additives. MOCA is used as an additive in the polyol blend with the purpose to give the resulting polymer

specific properties. Depending on the function MOCA has within the polymer, four uses can be differentiated:

- Curing agent
- Cross-linker
- Chain extender
- Pre-polymer

MOCA can be used as a curing agent for polyurethane resins, polyurethane elastomers, epoxy resins and epoxy urethane resins due to MOCA's content of amine groups.

MOCA is also used as a cross-linking agent where polymer chains are connected, creating an organised network structure. This makes the resulting polyurethanes very resistant to abrasion and adds thermal stability. These polyurethanes can be used in the production of machines, buildings, automobiles, airplanes, mining and sport equipment.

Polyurethanes containing MOCA have high thermal, physical and abrasion resistance and are therefore used, e.g., in construction, for wheels, cars, electric wire coating, safety belts and recently also in biomaterials such as pace makers and implants. MOCA is also used in polyurethane coatings which require good flexibility or abrasion, solvent, weathering and ultraviolet light resistance. MOCA as curing agent in the manufacture of castable urethane rubber products, such as shock absorption pads and conveyor belting, achieves specific performance properties such as high abrasion resistance, high tensile and tear strength, heat, fuel and solvent resistance, high load-bearing and good mechanical and dynamic properties [36].

Cobalt dichloride is used as intermediate in the synthesis of other inorganic cobalt compounds (e.g. cobalt dihydroxide, cobalt oxalate). For the majority of these uses (approximately 95%), the cobalt dichloride is used as an on-site isolated intermediate. Another 10% of cobalt dichloride is used as an intermediate in the synthesis of organic cobalt compounds (cobalt carboxylates). Further intermediate uses are the synthesis of vitamin B12 as well as the synthesis of pigments. As regards non-intermediate uses, small tonnages may be used for electroplating, animal food and veterinary products. Further non-intermediate use of CoCl_2 takes place in

humidity indicators used for military purposes and in standard solutions to determine colour in liquids [37].

1,2,3-trichloropropane is no longer marketed for use in consumer applications. There is no evidence from consultation that 1,2,3-TCP is still used directly as a solvent and this use was not included in available registration dossiers. Today, 1,2,3-TCP is used primarily as a building block for the synthesis of other products, such as:

- Pesticides,
- Chlorinated solvents (as intermediate, so it is assumed that no 1,2,3-TCP is used in articles),
- Monomer use (TCP is used as a chemical intermediate in the production of polysulfone liquid polymers and dichloropropene, synthesis of hexafluoropropylene, and as a crosslinking agent in the synthesis of polysulfides) (1,2,3-TCP seemed to be used as a monomer in the manufacturing of polymers. The lifecycle of 1,2,3-TCP ends in this synthesis. Therefore, no 1,2,3-TCP is used in articles.) [38-39].

1,2-benzenedicarboxylic acid, di-c7-11 -branched and linear alkyl esters (DHNUP) is based on information from European manufacturers of phthalates and The European Council for Plasticisers and Intermediates (ECPI), the substance seems not (anymore) to be manufactured in the EU or imported to the EU. The primary use of DHNUP is as a plasticizer for electrical and communication wire insulation [40].

1-methyl-2-pyrrolidone (NMP) has the descriptions of uses :

- Coatings (paints, printing inks);
- Cleaning products (polymer removers, paint strippers/cleaners);
- Agrochemicals;
- Electronic equipment manufacture;
- Petrochemical processing;
- Pharmaceuticals;
- Other uses.

The ranges of final products to which the coatings are applied appear to be hugely diverse, including for example:

- Decorative and protective waterborne paints;
- Metal coatings;

- Concrete coatings;
- Wood coatings and wood care products;
- Automotive paints;Parquet lacquers;
- Artists colours;
- Screen printing inks;
- Inkjet inks (industrial and general public);
- Pen inks;
- Non-stick bakeware/cookware.

NMP is not assumed to be present in articles as it is used as a solvent in coatings. The NMP thus evaporates following application.

For electronic equipment manufacture; NMP is used as a solvent for the electronics industry and producers of printed circuit boards. Blends of the substance with common solvents are reportedly used for the cleaning and degreasing of single-crystal silicon wafers for integrated circuits.

NMP is reportedly an important solvent for polyimides. The main applications for NMP use are as:

- A photoresist carrier solvent (solvent base for polymer mixtures) used at around 10-100 t per location/company.
- A photoresist stripper (cleaning/stripping to remove resist from wafers and photo masks during semiconductor manufacturing) used at around 10-100 t per location/company.
- In failure analysis (cleaning/stripping) used at < 5 t per location/company [41].

Hydrazine has the applications that have been identified as currently relevant to the EU include:

- in its hydrated form (in solution concentrations ready for end-use between 3% and 100%): synthesis of hydrazine derivatives – these may act as or find uses in products such as pharmaceuticals, agrochemicals, chemical blowing agents, paints, inks and organic dyes, reagents for the treatment of nuclear reactor waste, and others (literature provides details of a large range of different applications for derivatives, salts, etc. of hydrazine); use as a monomer in polymerisations and foaming agent for polymer foams (mostly

for polyurethane coatings and adhesives); use as a corrosion inhibitor in water treatment, mainly for the removal of dissolved oxygen and the adjustment of pH in the feedwater of boilers as well as for the removal of solids from steam generators; use as a reducing agent in the deposition of metals (nickel, chromium, tin and precious metals) on plastics and glass; use as a reducing agent in precious metal and basic metal recovery from metallic salt solutions and effluents; use as a reducing agent in purification of chemical reagents; use as a stabilising agent in aromatic amines (for subsequent paint/ink manufacture); use as a laboratory chemical reagent;

- in its anhydrous form (at high purity levels, >90%): use as a propellant for aerospace vehicles (satellite propulsion and upper stages of satellite launchers); use as a fuel in military (emergency) power units (for the F-16 fighter jets); use in gas generators for submarine rescue systems [42].

Strontium chromate is used by these sectors:

- formulation of strontium chromate containing mixtures (coatings such as paints, varnishes, oil-colors, inks, glues, adhesives, sealants, etc.) (for paints mainly as corrosion inhibitor and as pigments),
- colorant in manufactured polyvinyl chloride resins,
- industrial use of strontium chromate containing formulations (coatings and mixtures) in the aeronautic/aerospace sector,
- industrial use of strontium chromate containing formulations (coatings) in the coil coating sector of steel and aluminum,
- industrial use of strontium chromate containing formulations (coatings and mixtures) in the vehicle coating sector,
- fireworks and pyrotechnics manufacturing [43].

2-ethoxyethyl acetate is a volatile organic compound (VOC). At ground level, VOCs can react with other air pollutants contributing to the formation of potentially harmful concentrations of ozone in the lower atmosphere [18]. 2-EEA was mainly used as solvent in the chemical industry and for the formulation of paints, coatings, adhesives, lacquers, varnishes and some wood stains for industrial use. 2-EEA was also used as an intermediate in the chemical industry and as an industrial solvent and in automobile lacquers to retard evaporation and impart high gloss [44-45].

1,2-benzenedicarboxylic acid, di-c6-8-branched alkyl esters, c7-rich (DIHP) has the main former use of DIHP in the EU was as plasticiser in PVC and, the substance was largely used in PVC flooring.

The main reported uses of DIHP were:

- Plasticiser in PVC
- Plasticiser in sealants and printing inks.
- oil additive for engine oils
- adhesives

The following applications were listed for the use of DIHP as a plasticiser:

- Vinyl flooring, tile and carpet backing;
- Moulding and coating plastisols;
- Partial replacement for other low molecular weight plasticizers (e.g. DEHP) in extrusion, injection moulding and calendaring applications requiring improved processability [46].

Chromic acid, oligomers of chromic acid and dichromic acid, dichromic acid has mainly used in metal processes electrolysis, polishing etc. Besides it used as a fixing agent in wood preservatives. In small quantities it also used in manufacture of pigment, dye, catalyst and as an oxidizing agent [47].

Cobalt (II) carbonate applications are given in Table 2.2 and *cobalt (II) diacetate* applications are given in Table 2.3 [48-49].

2-Methoxyethanol (EGME) found a wide application as a solvent for many different purposes such as varnishes, dyes, and resins; chemical intermediate and solvent coupler of mixtures and water-based formulations. For cosmetics the use of EGME is forbidden. In addition, it can also be used as industrial processing aid in different areas (e.g. in the manufacture of medical devices). It is also used as an additive in airplane deicing solutions [50-51].

Chromium trioxide main uses are:

- metal finishing (for electroplating e. g. hard chrome plating, decorative or bright-chrome plating, conversion coatings, e.g. passivation of zinc, aluminium, cadmium and brass, pickling →[CrO₃ solution])

- manufacture of wood preservation products (biocidal agent (not relevant for REACH); fixing agent in waterborne wood preservatives)

Table 2. 2 : Identified use and/or activity sectors for cobalt carbonate.

| Use and/or Activity Sector | Further information |
|-----------------------------------|--|
| Manufacture of catalysts | Manufacture of catalysts: Hydrotreating; Oxidation catalyst; Hydrodesulphurisation; Fischer Tropsch (GTL) |
| Animal food supplement | Animal health: animal food supplement/ additive |
| Production of other chemicals | Production of other chemicals (intermediate): starting material in the manufacture of other chemicals, such as cobalt oxide, cobalt pigments and cobalt salts (for example cobalt difluoride is prepared commercially by the reaction of cobalt(II) carbonate with anhydrous hydrogen fluoride.) |
| Production of pigments | Production of pigments for decorating porcelains (intermediate). In addition, industry reports some references to direct use as pigment for decorating porcelain and clays. |
| Adhesion | Adhesion: ground coat frit(intermediate). |
| Other | Other: Additive to soils/ fertilizer: (in soil application the cobalt is readily assimilated into the plants and subsequently made available to the animals.) Veterinary medication to prevent and treat cobalt deficiency in ruminants (mainly intermediate) Temperature indicator |

Other uses of chromium trioxide are:

- catalyst manufacture,
- chromium dioxide manufacture,
- pigment manufacture,
- manufacture of paints, varnishes and inks putty (anticorrosive, dye),
- oxidant in organic chemistry,
- electronic component manufacturing (characterization of silicon wafers),
- production of polyethylene and other plastics (catalyst),
- metallurgy of nonferrous metals (elaboration of chromium metal),
- manufacture of soap, detergents and cleaning agents,
- manufacture of other organic basic chemicals,
- inorganic hardening agent layer of photosensitive galantine,
- manufacture of jewellery (production of synthetic sapphire),

- and there are some additional uses in research and development:
- hardening of microscopic preparation,
- oxidizer [52].

Table 2. 3 : Identified use and/or activity sectors for cobalt (II) diacetate.

| Use and/or Activity Sector | Further information |
|---|--|
| Manufacture of catalysts | Manufacture of catalysts Hydrotreating; Oxidation catalyst; Hydrodesulphurisation; Fischer Tropsch (GTL) |
| Production of other chemicals | Production of other chemicals (intermediate): feed materials for other chemicals |
| Surface treatment Alloys | Surface treatments(intermediate): anodizing (coloring of anodized aluminum profiles) Alloys (hard metals) (intermediate) |
| Production of pigments Dyes Adhesion Other | Production of pigments: ceramic, anodizing (intermediate) Pigments for decorating porcelains Pigment: anodizing (coloring of anodized aluminum profiles) Pigment for oil cloth or other dyes. Cobalt salts are used to improve the adhesion of rubber to steel. Other: bleaching agent for lacquers and varnishes Dryer in paint and varnish. |
| Animal food supplement | Animal health: animal food supplement/ additive |

Cobalt (II) sulphate data on use applications are given in Table 2.4 [53].

Cobalt(II) dinitrate data on use applications are given in Table 2.5 [54].

2-Ethoxyethanol (EGEE) is processed to intermediates such as the 2-ethoxyethanol tert-butyl ether (1-Ethoxy-2-tert-butoxyethane) in chemical industry. The smaller part (20 %) is used as industrial solvent. Besides the industrial use as intermediate and solvent, EGEE was used for the formulation of paints, lacquers, varnishes and printing inks. An additional use for 2-ethoxyethanol as anti-freeze additive for aviation fuels and for clearing runways is obsolete now [55].

Table 2. 4 : Identified use and/or activity sectors for cobalt sulphate.

| Use and/or Activity Sector | Further information |
|---|--|
| Production of other chemicals | Production of other chemicals (intermediate): feed materials for other chemicals |
| Manufacture of catalysts Manufacture of driers | Manufacture of drier for lithographic inks (mainly intermediate) Drier for paints and linoleum (mainly intermediate) Manufacture of catalysts |
| Surface treatments Corrosion prevention Other | Surface treatments: anodizing, electro-deposition, non-electro deposition (mainly intermediate) Electroplating baths (Cobalt is plated from chloride, sulphate, fluoborate, sulfamate, and mixed anionic baths. Cobalt alloyed with nickel, tungsten, iron, molybdenum, chromium, zinc, and precious metals are plated from mixed metal baths. Corrosion protection agent (mainly intermediate) Other: Batteries: Cobalt sulphate supplies Li ion batteries use for automotive market (hybrid electric vehicle and electric vehicle) and storage (for intermittent renewable energy generation; photovoltaic and wind) applications (mainly intermediate) Additive to soils/ fertilizer: could be considered as an additive to fertilizers (i.e. trace element) to facilitate the absorption of nitrogen by specific plants (e.g. legumes) Veterinary medication Magnetic recording materials |
| Production of pigments Decolourising | Production of pigments: ink, ceramic, anodizing, textiles, glass, dyes Pigments for decorating porcelains;in ceramics, glazes and enamels to protect from discoloring, possibly used as bleaching agent in sanitary ceramics; Manufacture of organic textile dyes (cobalt complexes of azo dye derivates)) |
| Animal food supplement | Animal food supplement |

Table 2.5 : Identified use and/or activity sectors for cobalt dinitrate.

| Use and/or Activity Sector | Further information |
|-----------------------------------|--|
| Manufacture of catalysts | <p>Manufacture of catalysts and use as catalyst (mainly intermediate)</p> <p>Cobalt dinitrate is consumed in the course of the catalyst manufacturing process and is not present in the final catalyst according to industry.</p> <p>Hydrotreating catalyst and hydrodesulfurization catalyst (preparation of refining and petrochemical catalysts).</p> <p>Catalyst for Fischer Tropsch (GTL) reaction (conversion from gas to liquid fuel): Cobalt compounds are used as catalysts in several processes of lesser industrial importance. Fischer-Tropsch catalysts produced from cobalt salts produce less methane than the corresponding iron catalysts. The chemistry of carboxylation reactions catalyzed in the presence of cobalt is also rich.</p> |
| Production of other chemicals | Production of other chemicals (intermediate): feed materials for other chemicals |
| Surface treatments | Surface treatments: Anodizing, Electro-deposition, Non-electro deposition (mainly intermediate) |
| Batteries Other | <p>Batteries:</p> <p>Cobalt dinitrate compounds are used in the manufacture of the nickelbased electrodes of several alkaline rechargeable battery technologies. These are essentially Ni-MH (nickel metal hydride) used in hybrid vehicles and Ni-Cd used in specific industrial applications (mainly intermediate).</p> <p>Other:</p> <p>Ceramics: Cobalt dinitrate can be used for pigment production in ceramic industry. As pigment: decorating stoneware and porcelain</p> <p>Sympathetic (invisible) inks: The information printed by common laser printers equipped with invisible ink is invisible in normal condition. It can not be copied and just can be seen under the UV light or our special readers.</p> |

Disodium tetraborate, anhydrous is used in:

- Household products (used in various household laundry and cleaning products),
- Buffer (used in biochemical and chemical laboratories to make buffers, e.g. for gel electrophoresis of DNA),

- Flux (A mixture of borax and ammonium chloride is used as a flux when welding iron and steel),
- Putty (a rubbery polymer sometimes called flubber, gluep or glurch can be made by cross linking polyvinyl alcohol with a borax. Making flubber from polyvinyl alcohol based glues),
- Food additive,
- Ingredient in enamel glazes,
- Component of glass, pottery, and ceramics,
- Borax can be used as an additive in ceramic slips and glazes to improve fit on wet, greenware, and bisque,
- Fire retardant,
- Anti-fungal compound for fiberglass and cellulose insulation,
- Anti-fungal foot soak,
- Physical insecticide to kill ants, cockroaches and fleas,
- Precursor for sodium perborate monohydrate that is used in detergents, as well as for boric acid and other borates,
- Tackifier ingredient in casein, starch and dextrin based adhesives,
- Precursor for boric acid, a tackifier ingredient in polyvinyl acetate, polyvinyl alcohol based adhesives,
- Used to make indelible ink for dip pens by dissolving shellac into heated borax,
- Swimming pool buffering agent to control the pH,
- Neutron absorber, used in nuclear reactors and spent fuel pools to control reactivity and to shut down a nuclear chain reaction,
- As a micronutrient fertilizer to correct boron-deficient soils,
- To clean the brain cavity of a skull for mounting,
- To color fires with a green tint [56].

Ammonium dichromate is mainly used as an oxidising agent. It is also used as intermediate in the synthesis of fine and bulk large scale chemicals. Furthermore it is used as laboratory chemical. Other known uses are in the manufacture of photosensitive screens and as mordant in the manufacture of textiles [57-59].

Tetraboron disodium heptaoxide, hydrate, disodium tetraborate and tetraboron disodium heptaoxide form the same compounds in aqueous solutions. Uses include a multitude of applications, e.g. in detergents and cleaners, in glass and glass fibres, ceramics, industrial fluids, metallurgy, adhesives, flame retardants, personal care products, biocides, fertilisers [57].

Potassium dichromate is for metal surface treatment and coating of metals as corrosion inhibitor. Potassium chromate is also used as intermediate in the synthesis of other substances. It is further used as textile mordant, as laboratory analytical agent, for cleaning of laboratory glassware, in the manufacture of other reagents and as oxidising agent in photolithography [57-60].

Trichloroethylene main use is in the vapor degreasing of metal parts. It is also used as an extraction solvent for greases, oils, fats, waxes, and tars, a chemical intermediate in the production of other chemicals, and as a refrigerant, in consumer products such as typewriter correction fluids, paint removers/strippers, adhesives, spot removers, and rug-cleaning fluids [61].

Sodium chromate is mainly used as an intermediate in the manufacture of other chromium compounds as well as a laboratory analytical agent [57].

Potassium chromate is used in leather finishing, as a textile mordant, and in enamels and pigments, as a corrosion inhibitor for treatment and coating of metals, as a colouring agent in ceramics. It is used as an analytical reagent and as an indicator in the laboratory [57-58].

Boric acid, also called hydrogen borate or boracic acid or orthoboric acid or acidum boricum, is a weak acid of boron often used as an antiseptic, insecticide, flame retardant, as a neutron absorber, and as a precursor of other chemical compounds. The primary industrial use of boric acid is in the manufacture of monofilament fiberglass usually referred to as textile fiberglass. Textile fiberglass is used to reinforce plastics in applications that range from boats, to industrial piping to computer circuit boards. Boric acid is used in the production of the glass in LCD flat panel displays [62].

Acrylamide is almost exclusively used for the synthesis of polyacrylamides, which are used in various applications, in particular in waste water treatment and paper processing. Minor uses of acrylamide comprise the preparation of polyacrylamide

gels for research purposes and as a grouting agent in civil engineering. Some acrylamide is used in the manufacture of dyes and the manufacture of other monomers [63-64].

Lead chromate molybdate sulphate red (C.I. Pigment Red 104) is used as a colouring, painting and coating agent in sectors such as the rubber, plastic and paints, coatings and varnishes industries. Applications comprise the production of agricultural equipment, vehicles and aircraft as well as road and airstrip painting [65].

Lead chromate is used for manufacturing pigments and dyes, and as a pigment or coating agent in industrial and maritime paint products or varnishes. Further potential uses may be associated with the formulation of detergents and bleaches, photosensitive materials, the manufacture of pyrotechnic powder or the embalming / restoring of art products [65].

Anthracene oil; Anthracene oil, anthracene pastes, distn, lights; Anthracene oil, anthracene paste, anthracene fraction; Anthracene oil, anthracene-low; Anthracene oil, anthracene paste are mainly used in the manufacturing of other substances, such as anthracene and carbon black. They may also be used as reducing agents in blast furnaces as components in bunker fuel, for impregnating, sealing and corrosion protection [65].

2,4-Dinitrotoluene is primarily used as a chemical intermediate in the synthesis of toluene diisocyanate (4-methyl-m-phenylenediisocyanate). 2,4-Dinitrotoluene is hydrogenated to yield TDA and this diamine is reacted with phosgene to yield TDI, which is used to make flexible polyurethane foams. No clear indication of the amount of DNT used in or supplied to the explosives sector [66].

Tris(2-chloroethyl)phosphate is mainly used as an additive plasticiser and viscosity regulator with flame-retarding properties for acrylic resins, polyurethane, polyvinyl chloride and other polymers. Other fields of application are adhesives, coatings, flame resistant paints and varnishes. The main industrial branches to use TCEP are the furniture, the textile and the building industry [65].

Aluminosilicate Refractory Ceramic Fibres and ***Zirconia Aluminosilicate Refractory Ceramic Fibres*** (Annex VI, part 3, table 3.1 of Regulation (EC) No 1272/2008) are used for high-temperature insulation, almost exclusively in industrial

applications (insulation of industrial furnaces and equipment, equipment for the automotive and aircraft/aerospace industry) and in fire protection (buildings and industrial process equipment) [65].

Pitch, coal tar, high temp. is mainly used in the production of electrodes for industrial applications. Smaller volumes are dedicated to specific uses such as heavy duty corrosion protection, special purpose paving, manufacture of other substances and the production of clay targets [65].

Lead sulfochromate yellow (C.I. Pigment Yellow 34) is used as a colouring, painting and coating agent in sectors such as the rubber, plastic and paints, coatings and varnishes industries. Applications comprise the production of agricultural equipment, vehicles and aircraft as well as road and airstrip painting. The substance is further used for camouflage or ammunition marking in the defence area [65].

Diisobutyl phthalate is used as a specialist plasticiser and frequently as a gelling aid in combination with other plasticisers and as plasticiser for nitrocellulose, cellulose ether and polyacrylate and polyacetate dispersions. These are used in paints, lacquers, varnishes, paper, pulp and boards, as adhesives, binding agents, softeners and viscosity adjusters. DIBP is also used in coatings, e.g. antislip coatings, and in epoxy repair mortars. As a plasticiser in dispersion glues and printing inks DIBP is applied in paper and packaging for food (e.g. rice, baking mixtures, cheese, bread, nuts) and bottled water. Due to similar application properties it may be used as a substitute for dibutyl phthalate (DBP) [67].

Sodium dichromate is used in:

- Production chromium (III) oxide (intermediate);
- Production of chromium (VI) pigments (intermediate);
- Anticorrosion additive in coatings;
- Production of chromium metal (intermediate);
- Metal finishing;
- Production of tanning salts (intermediate);
- Production of montan wax;
- Production of vitamin K;
- Mordents for wool dyes [68].

5-tert-butyl-2,4,6-trinitro-m-xylene (musk xylene) belongs to the family of synthetic musks which are substances used to emulate the aroma produced by natural musk. Musk ingredients are a significant ingredient for fragrance formulation both as fragrance and fragrance enhancers used in most fragrance mixtures for detergents, fabric softeners, fabric conditioners, cleaning agents, air fresheners and other household products [69].

4,4'- Diaminodiphenylmethane (MDA) has more than 98% of the total production volume is processed to methylenediphenyl diisocyanate (MDI). MDI is further used for polyurethane production. The main applications for polyurethane are as follows,

- adhesives/sealants (7%);
- appliances (7%);
- automotive applications (16%);
- binders (2%);
- building construction (22%);
- coatings (9%);
- elastomers (7%);
- footwear (8%) and
- furniture/bedding (23%).

Apart from its use in the synthesis of MDI, the RAR (EC, 2001) identifies the following uses of MDA:

- Hardener in epoxy resins;
- Hardener in adhesives;
- Intermediate in the manufacture of high performance polymers;
- Processing to 4-4'methylenebis(cyclohexaneamine) (H12MDA) [70].

Bis(tributyltin)oxide (TBTO) has used in hospitals and other public buildings, and in industrial plants to control mould and bacterial growth in damp areas not associated with food preparation or storage; to prevent odours in garbage pails and equipment; and to control athletes foot in shower areas and locker rooms. It has also been used in manufacturing processes (e.g., leather goods, textiles, wood, and plastics) and to mothproof stored garments [71].

Triethyl arsenate is used in specialised doping applications. Doping is a routine process in fabricating semiconductor devices. In the production of electronic components such as semi-conductors triethyl arsenate can be considered as an intermediate [72].

Dibutyl phthalate (DBP) is a specialist, fast fusing plasticiser. By itself it is too volatile for PVC applications and it is used in PVC as a gelling aid in combination with other high molecular weight plasticisers. Current uses of DBP:

Gelling aid in combination with other plasticisers in plastics. DBP is used in PVC Rubbers. DBP is used in some polychloroprene rubber and nitrile rubber, but not in all polychloroprene (neoprene) or nitrile rubbers.

- DBP is used extensively in the adhesives industry to plasticise polyvinyl acetate (PVA) emulsions;
- Epoxy resins;
- In the coatings industry as a primary plasticiser-solvent for nitrocellulose lacquers;
- Grouting agents, used to reduce water leakages in tunnels, sewer systems, buildings etc.
- Other applications:
 - Solvent for many oil-soluble dyes, insecticides, peroxides and other organic compounds;
 - Antifoam agent and as a fibre lubricant in textile manufacturing;
 - Used in compounding flavours;
 - Printing inks, polishing agents, corrosion inhibitor materials;
 - Use in PP (polypropylene) catalytic systems [73].

Diarsenic pentaoxide and *diarsenic trioxide* are;

- Used in the dyeing industry;
- Used in metallurgy (to harden copper, lead or gold in alloys);
- Used for manufacturing special glass;
- Used for intermediate for other arsenic compounds;
- Used in wood preservatives [74-75].

Anthracene is a basic substance for production of anthraquinone, dyes, pigments, insecticides, wood preservatives and coating materials. Anthracene is a nucleus for polymer soluble pigments. Anthracene forms reversible photodimer through the 9-10- positions in response to light and provides photochromic applications. Anthracene family compounds are base materials for colorings. They have useful functions such as light and temperature sensitivity, heat resistance, conductivity, emittability, and corrosion resistance. Due to pi-electron cloud overlaps, anthracene exhibits semiconductor property. Organic semiconductors have some merits of self radiation, flexibility, light weight, easy fabrication, and low cost. They have been investigated as organic electroluminescence materials for the applications in organic solar cells, biosensitizers and display devices such as OLED(Organic Light Emitting Diode), OTFT(Organic Thin Film Transistor), Wearable Display, and e-paper [76].

Alkanes, C10-13, chloro (Short Chain Chlorinated Paraffins) have used as lubricants in the metal working industry. The other uses leather greasing, softener in PVC and chlorinated rubber, flame protection in plastics and textiles [77-78].

Lead hydrogen arsenate has previously been used as a pesticide [79].

Benzyl butyl phthalate (BBP) is one of a number of substances used as plasticiser in PVC and other polymer materials. It is used widely by the flooring industry because it adds surface properties to flooring materials that minimise maintenance and give it a prolonged life BBP the end-product uses of BBP are as follows:

- Flooring (both calendered and spread coated flooring);
- Wall covering;
- Coating of leather and textiles (upholstery, shoe uppers, wallets/bags, luggage);
- Packaging films;
- Sealants (polysulphide based, polyurethane based or acrylic-based) for insulating;
- double glazing and other applications;
- Paints for car care and construction (acrylic lacquers and other);
- Inks for paper and board;
- Adhesives (polyvinyl acetate and other);
- Miscellaneous (hard PVC, nitrile rubber and other).

BBP is not permitted for use in toys and childcare articles (Directive 2005/84/EC) or in cosmetics [80].

Hexabromocyclododecane (HBCDD) is used solely as an additive flame retardant in the following main product types:

- Expanded Polystyrene (EPS);
- Extruded Polystyrene (XPS);
- High Impact Polystyrene (HIPS);
- Polymer dispersion for textiles.

The main uses of EPS are insulation panels/boards in the construction sector and automobile cushions for children. Minor uses are packaging material and props for exhibitions, films or similar. XPS is mainly used as a thermal insulation in buildings (residential, industrial and agricultural), civil engineering applications, cold stores and vehicles. The use of HBCDD in HIPS is mainly for video and stereo equipment, distribution boxes for electrical lines in the construction sector [81].

Bis (2-ethylhexyl)phthalate (DEHP) is widely used as a plasticiser in polymer products, mainly PVC. DEHP is a plasticiser which offers a good all-round performance and is therefore used for a many general purpose products including building material such as flooring, cables, profiles and roofs, as well as medical products such as blood bags and dialysis equipment. The main end-product uses of DEHP are as follows:

- Flooring:
 - PVC flooring (with PVC surface);
 - Carpets with PVC back-coating;
 - Cork with PVC top-coating or back-coating ;
- Wall covering;
- Roofing;
- Film/sheet and coated products:
 - Curtains, blinds, table linen, etc.;
 - Packaging;
 - Tape and self-adhesive foils;
 - Office supplies (ring binders, files, slip cases, etc.);

- Toys (swimming pools, rubber beach toy, beach balls, etc.).
- Medical bag/sheet devices;
- Bottom sheets for hospitals.
- Wires and cables;
- Hoses and profiles;
 - Garden hoses and tubes;
 - Hoses and tubes in industry;
 - Profiles of windows and electrical products;
 - Medical tubing.
- Coated fabric;
 - Upholstery and car seats (synthetic leather);
 - Luggage;
 - Rainwear;
 - Tarpaulins;
 - Water beds.
- Moulded product;
 - Footwear;
 - Adult toys (DEHP is not permitted in toys for children);
- Car undercoating;

Non-polymer applications:

- Adhesives;
- Lacquers and paints;
- Printing inks (see comment below);
- Sealants (glass insulation, construction);
- Ceramics.

DEHP is not permitted for use in toys and childcare articles (Directive 2005/84/EC) or in cosmetics [82].

2.3.4 Potential usages of SVHCs in white appliances and consumer electronics

APPENDIX B summaries the potential usages of SVHCs in white appliances and consumer electronics.

2.3.5 SVHC management in white appliances and consumer electronics

In this study, we will be discussing only one set of the REACH requirements -- SVHC in articles. In most cases, this is the only requirement that impacts electronic manufacturers.

Organizations that manufacture or import products containing an SVHC have compliance obligations. If the product is a substance or mixture, the SVHC must be identified in material safety data sheets. For an article with an SVHC present at greater than 0.1% weight over weight, there are mandatory communication obligations to customers. If manufacture or import of the SVHC is over 1 ton per year there are also 'Notification' obligations to ECHA. Once an SVHC has become restricted, an organization must request and be granted 'Authorization' from ECHA to continue use after the sunset date [83].

Examples of SVHC declarations of some white appliances and consumer electronics sectors for communication obligations shown in Table 2.6-10 [84].

Table 2. 6 : SVHC declaration form example 1.

| Products | Substances of Very High Concern (SVHC) | |
|--|--|------------------------|
| | Substance name ¹⁾ | EC Number (CAS Number) |
| Laptops and Tablet PC's with accessories, such as AC cable, AC adapter, etc. ²⁾ | Bis (2-ethyl(hexyl)phthalate) (DEHP) in AC-cable | 204-211-0 (117-81-7) |

²⁾ calculation is based on the total weight % of all parts delivered with the laptop

Table 2. 7 : SVHC declaration form example 2.

| | |
|---|---|
| TV and Home Projectors | Among Substances of Very High Concern (SVHC) identified in the most recent Candidate List exceeding 0.1% weight by weight per article, DEHP (^{**}) may be contained in the cables of those Sony products. |
| VAIO® Computing | |
| PlayStation® | |
| Digital Imaging Digital cameras, camcorders, photo frames, printers, e-books | |
| Audio Home, car, mobile, headphones | |
| Video Blu-ray Disc, DVD, Home Cinema | Among Substances of Very High Concern (SVHC) identified in the most recent Candidate List exceeding 0.1% weight by weight per article, DEHP (^{**}) may be contained in the cables of those Sony products and lens hoods for HDV camcorders. |
| Accessories e.g. Camcorder accessories, Personal audio accessories, DVD writers, PC peripherals | |
| Broadcast, Business and Professional Products e.g. Broadcast & Pro. A / V, Projectors, Public Displays, Video Security, Industrial Cameras, Video Conferencing, Digital Photography, Medical, IT Storage, Manufacturing Solutions | No Substances of Very High Concern (SVHC) in the most recent Candidate List are contained in concentrations above 0.1% weight by weight in the articles. |
| Batteries | |
| Recording Media Tape, disc (Blu-ray Disc, DVD, CD, MFD) | |
| Memory Device Memory Stick, SD, USB FD, AIT drive | |
| Print Media | |
| Internal Bulk Drive Separately sold internal DVD/Blu-ray drive | |

(^{*}) meeting the criteria in Article 57 and identified in accordance with Article 59(1) in concentration above 0.1% w/w - as published 28th October 2008 and most recently amended on 13th January 2010 and 30th March 2010.

(^{**}) **DEHP**: Bis(2-ethylhexyl)phthalate; CAS No. 117-81-7; EC No. 204-211-0; alternative names: Di(2-ethylhexyl)phthalate, Diethylhexylphthalate

Table 2.8 : SVHC declaration form example 3.

| Substance | CAS No | Product Group affected | Application | Safe use information |
|--------------------------------------|-----------|---|-----------------------------|--|
| Bis (2-ethyl(hexyl)phthalate) (DEHP) | 117-81-7 | PVC power cords and cables in Samsung Electronics products may potentially contain DEHP above 0.1% by weight. | Plasticizer in PVC cable | This product and its accessories are not a toy and should not be sucked or placed in the mouth. Please keep out of reach of very young children. In accordance with the European WEEE Directive this product and its electronic accessories (e.g. charger, USB cable) should not be disposed of with other household waste at the end of their working life. Please see WEEE instructions supplied with the product on correct disposal and recycling channels. |
| Diarsenic trioxide | 1327-53-3 | Electric Cooktop | Fining agent in Glass plate | In accordance with the European WEEE Directive this product and its electronic accessories should not be disposed of with other household waste at the end of their working life. Please see WEEE instructions supplied with the product on correct disposal and recycling channels. |

Table 2.9 : SVHC declaration form example 4.

Monitors

| Product / Part Name | Substance Name | CAS Number (where available) |
|---|--------------------------------------|------------------------------|
| LCD Display Power Cord CRT Display Power Cord Display Audio Cable Display DVI Cable Display DVI Dual Link Cable Display HDMI Cable Display Port Cable Display USB Cable Display VGA Cable Display VGA to DVI Cable | Bis (2-ethyl(hexyl)phthalate) (DEHP) | 117-81-7 |
| Flat Panel Monitor Quick-Release Mount Flat Panel Speaker Bar Integrated Work Center Stand LCD Display Head LCD Display Stand Monitor Advanced Profiling Solution Monitor Hood Kit Privacy Filter | None | Not Applicable |

Table 2. 10 : SVHC declaration form example 5.

For dishwashers:

| | |
|------------------------------|---|
| Name of the substance(s) | Bis (2-ethyl(hexyl)phthalate) (DEHP) |
| CAS-No: | 117-81-7 |
| EINECS-No: | 204-211-0 |
| Concentration in % by weight | 0.2 % |
| Information for safe use | This product and its accessories are not a toy and should not be sucked or placed in the mouth. Please keep out of reach of children. |

Analyse reports can be used instead of SVHC declarations. It is a safe and certain way for information obligation. There are accredited laboratories which can test all SVHCs. An example page of SVHC a test report shown in Figure 2.3 [85].



RESULTS

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REPORT : TURA110043134

13 May, 2011

| Test Method | Result | Requirements |
|-------------|--------|--------------|
|-------------|--------|--------------|

3. Organic substances, in %

Test Equipment : GC-MS / HPLC / GC-ECD
 Detection Limit : 0.02%; Anthracene: 0.0002%

| Substance | CAS-No. | CS 1 | CS 2 | CS 3 |
|--|------------|--------------|--------------|--------------|
| Anthracene | 120-12-7 | Not Detected | Not Detected | Not Detected |
| 4,4'- Diaminodiphenylmethane | 101-77-9 | Not Detected | Not Detected | Not Detected |
| Dibutylphthalate (DBP) | 84-74-2 | Not Detected | Not Detected | Not Detected |
| 5-tert-butyl-2,4,8-trinitro-m-xylene (musk xylene) | 81-15-2 | Not Detected | Not Detected | Not Detected |
| Bis(2-ethylhexyl)phthalate (DEHP) | 117-81-7 | Not Detected | Not Detected | Not Detected |
| Hexabromocyclododecane (HBCDD) | 25637-99-4 | Not Detected | Not Detected | Not Detected |
| Short chain chloroparaffins C ₁₀ -C ₁₃ | 85535-94-8 | Not Detected | Not Detected | Not Detected |
| Tributyl tin oxide | 56-35-9 | Not Detected | Not Detected | Not Detected |
| Benzylbutylphthalate (BBP) | 85-98-7 | Not Detected | Not Detected | Not Detected |
| 2,4-Dinitrotoluene | 121-14-2 | Not Detected | Not Detected | Not Detected |
| Diisobutylphthalate | 84-89-5 | Not Detected | Not Detected | Not Detected |
| Tris(2-chloroethyl)phosphate | 115-96-8 | Not Detected | Not Detected | Not Detected |
| Acrylamide | 79-06-1 | Not Detected | Not Detected | Not Detected |
| Trichloroethylene | 79-01-8 | Not Detected | Not Detected | Not Detected |
| 2-Methoxyethanol | 109-88-4 | Not Detected | Not Detected | Not Detected |
| 2-Ethoxyethanol | 110-80-5 | Not Detected | Not Detected | Not Detected |

| | | | | |
|---|--|--------------|--------------|--------------|
| Anthracene oils and anthracene pastes (Analytically determined via the concentration of anthracene) | 90640-80-5 91995-17-4 91995-15-2 90640-82-7 90640-81-6 | Not Detected | Not Detected | Not Detected |
| Coal tar (Analytically determined via the concentration of the sum of the 12 polycyclic aromatic hydrocarbons) | 65999-93-2 | Not Detected | Not Detected | Not Detected |

Calculated for the whole product the detected amount in % is:

| | | | | |
|--|----|----|----|----|
| | -- | -- | -- | -- |
|--|----|----|----|----|

Figure 2.3 : SVHC analyse report.

Although the mass percent of the article can sometimes ‘hide’ an SVHC from reporting, manufacturers and their downstream operators should note that articles include spare parts or individual pieces that may be shipped unassembled in the same shipping package. For example, a detachable power cable shipped with an electronic product is considered a separate article and must comply with the SVHC communication obligations. A battery or any other part that is not pre-assembled is similarly a separate article [83].

Other than communication obligation, companies have to fulfil their notification to ECHA obligation if their products meet the 0.1% and 1 ton/year criteria. As known notification is not required if the SVHC has already been registered for same use before. For this exemption, companies should provide the registration information from their suppliers. An example of DEHP registration information shown in Figure 2.4 [86].

| | | |
|--|---|-------------------------|
| Substance name | : Dioctyl phthalate | |
| Cas number | : 117-81-7 | |
| EC number | : 204-211-0 | |
| Registration reference number | : 01-2119484611-38-0016 | |
| | | |
| EC number: 204-211-0 | bis(2-ethylhexyl) phthalate (IUC4 DSN 3297) | CAS number: 117-81-7 |
| | | |
| 9.4 Exposure scenario 4: Service life of DEHP used as plasticiser in articles | | |
| The exposure of general population to DEHP used as plasticiser in articles has been extensively assessed by the European, American and Canadian authorities : the latest reviews in Europe were concluded in 2008 by the European Chemical Bureau (European Union Risk Assessment Report) and in 2008 by the Scientific Committee on Emerging and Newly Identified Health Risks. In the European Union Risk Assessment Report, different scenarios were identified : | | |
| <ul style="list-style-type: none"> - exposure by food contact materials : is no longer considered in this CSR due to the restriction of use of DEHP in food contact articles - toys and child-care articles : is no longer considered in this CSR due to the restriction of use of DEHP in toys - Oral exposure - Indoor air (building materials) - Gloves (clothing, gloves and footwear) - Dermal exposure - Car interior | | |
| The following type of articles were reported by downstream users in a survey carried out in 2009 (Cadogan 2010 b): | | |
| <ul style="list-style-type: none"> - medical devices (addressed under Exposure Scenario 5) - wire and cables - hoses - construction - roofing sheet - footwear - film and sheet - Packaging films - Automotive - Office devices - Tarpaulins | | |

Figure 2.4 : Registration information of DEHP.

2.4. SVHC Additives Which are Used in Manufacturing of Polymeric Materials

Polymer uses wide variety of chemicals in order to bring it in the form that it can be used as a component in the preparation of a variety of products or the coating to variety of articles in the market. In order to restrict the use of such substances ECHA has prioritized few hazardous chemicals under the heading Substances of Very High Concern [87].

The SVHC list includes performance chemicals such as plasticizers, flame retardants, and various functional additives added intentionally or as contaminants due to the use of recyclates [83].

2.4.1 SVHC additives of polymers in white appliances and consumer electronics

Plastics, resins, adhesives, paints, desiccants and flame retardants all pose a fairly significant risk of containing one or more SVHC. Several of the SVHC on the Candidate List may be found in white appliances and consumer electronics [64].

The other polymer that used in white appliances and electronics (especially in refrigerators) is polyurethane foam. The following SVHCs may be contained in polyurethane (PU) foam parts [87]:

- 2,4-Dinitrotoluene: used in the production of toluene diisocyanate which is used to produce flexible PU foams.
- 4,4'- Diaminodiphenylmethane: used in the production of MDI for polyurethane manufacture [70].

Following substances can be used as paint additives and because of these reasons they can be found in colorful parts of white appliances and electronic equipments [87].

- Lead chromate
- Lead chromate molybdate sulphate red
- Lead sulfochromate yellow
- Cobalt dichloride
- Anthracene

A specific SVHCs can be used as flame retardant in polymers:

- Hexabromocyclododecane (HBCDD) : Electric and electronic equipment use is in styrenebased polymers. Product packagings are articles that are easily

overlooked for REACH SVHC obligations and EPS is a very common packaging material in white appliances and consumer electronics sector.

The plasticizers is most frequently appearing group of SVHCs. Following phthalate based substances are used as a plasticizer in manufacturing of articles made of PVC especially.

- 1,2-Benzenedicarboxylic acid, di-C6-8-branched alkyl esters, C7-rich
- 1,2-Benzenedicarboxylic acid, di-C7-11-branched and linear alkyl esters
- Dibutyl phthalate (DBP)
- Bis (2-ethylhexyl)phthalate (DEHP)
- Benzyl butyl phthalate (BBP)
- Diisobutyl phthalate (DIBP)

Bis (2-ethylhexyl)phthalate (DEHP) is the most common plasticizer used in PVC [64]. In consequence of PVC is a commonly used plastic in white appliances and consumer electronics sector (in cables, power cords, hoses, gaskets etc.) the plasticizers specified above can be met typically.

2.5 Analyzing of Phthalates in PVC

Phthalic acid esters (phthalates) are the most commonly used plasticizers in PVC based products due to their compatibility and softening capability. Products and materials may be tested for phthalates using analytical test methods. Selecting the correct sample preparation and analytical test method is critical for achieving accurate test results. The phthalates must be fully extracted from the base material otherwise the test results will be inaccurate, but the test strategy must also be cost efficient. This requires the use of clever test strategies to maximize the relevant information with a minimum numbers of tests [83].

The identification and quantitation of phthalates requires an analytical technique which can separate each phthalate from other additives and from the plastic matrix itself. Gas chromatography/mass spectrometry (GC/MS) (FID or SIM method) is an excellent instrumental platform for this analysis. The gas chromatograph separates analytes, while the mass spectrometer response is correlated to the amount of phthalate and will confirm the identification [88]. HPLC and UPLC could be the other uncommon methods to analyse of phthalates [89].

2.5.1 GC/MS method

Gas chromatography mass spectrometry (GC/MS) is an instrumental technique, comprising a gas chromatograph coupled to a mass spectrometer (MS), by which complex mixtures of chemicals may be separated, identified and quantified [90].

The combination of the two components into a single GC/MS system forms an instrument capable of separating mixtures into their individual components, identifying, and then providing quantitative and qualitative information on the amounts and chemical structure of each compound [91].

In order for a compound to be analysed by GC/MS it must be sufficiently volatile and thermally stable. Samples are usually analyzed as organic solutions consequently materials of interest need to be solvent extracted and the extract subjected to various 'wet chemical' techniques before GC/MS analysis is possible [90].

There are a number of different possible GC/MS configurations, but all share common types of components. There must be some way of getting the sample into the chromatogram, an *injector*. There must be a *gas chromatograph* with its carrier gas source and control valving, its temperature control oven and microprocessor programmer, and tubing to connect the injector to the column and out to the mass spectrometer interface. There must be a *column* packed with support and coated with a stationary phase in which the separation occurs. There must be an *interface* module in which the separated compounds are transferred to the mass spectrometer's ionization source without remixing. There must be the *mass spectrometer* system, made up of the ionization source, focusing lens, mass analyzer, ion detector, and multistage pumping. Finally, there must be a *data/control* system to provide mass selection, lens and detector control, and data processing and interfacing to the GC and injector (see Fig. 2.5) [91].

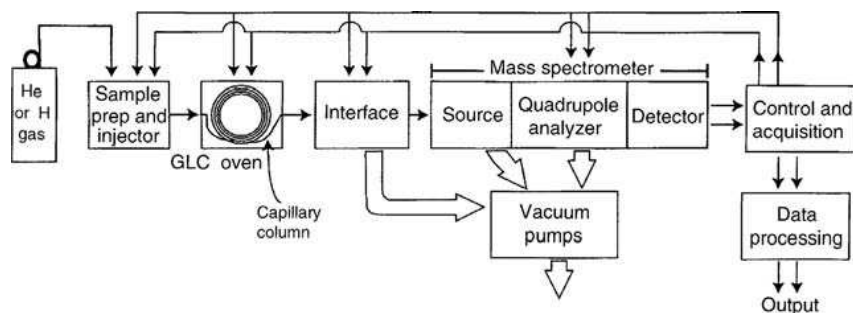


Figure 2.5 : A typical GC/MS system diagram.

An injector port (see Fig. 2.6) is necessary for introducing the sample at the head of the column. Commercial gas chromatographs often allow for both split and splitless injections when alternating between packed columns and capillary columns [92].

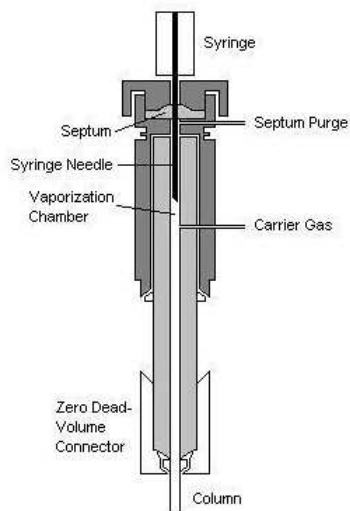


Figure 2.6 : A cross-sectional view of a microflash vaporizer direct injector.

The gas chromatograph, Figure 2.7, is basically a temperature-controlled oven designed to hold and heat the GC column. Carrier gas, usually either nitrogen, helium, or hydrogen, is used to sweep the injected sample onto and down the column where the separation occurs and then out into the mass spectrometer interface [91].

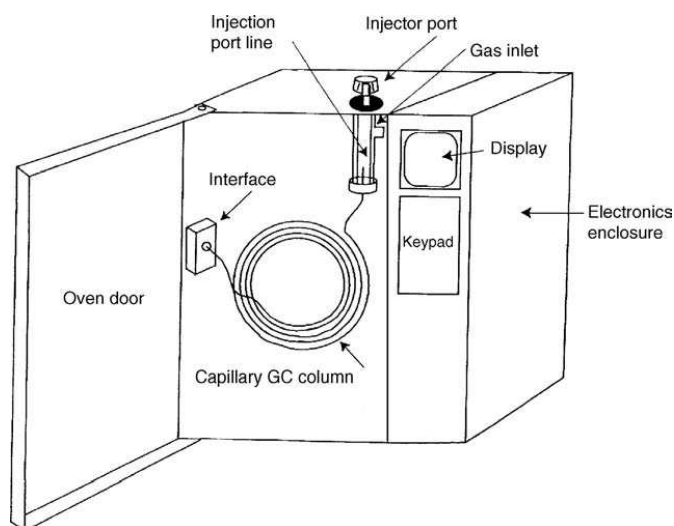


Figure 2.7 : Gas chromatograph.

The thermostatted oven serves to control the temperature of the column within a few tenths of a degree to conduct precise work. See the effect of column temperature on the shape of the peaks in Figure 2.8.

In the temperature programming method, the column temperature is either increased continuously or in steps as the separation progresses. The analysis begins at a low temperature to resolve the low boiling components, increases during the separation to resolve the less volatile, high boiling components of the sample. Rates of 5-7 °C/minute are typical for temperature programming separations [92].

Different types of columns can be applied for different fields. Depending on the type of sample, some GC columns are better than the others.

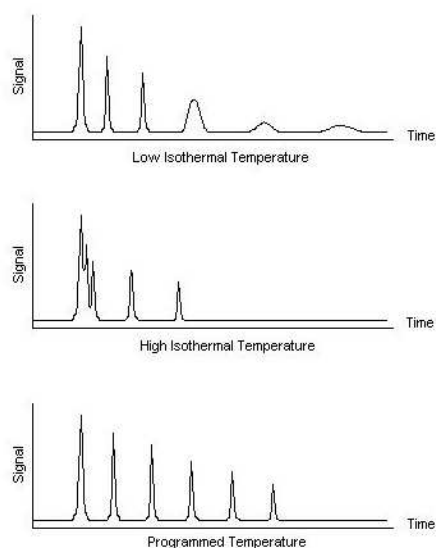


Figure 2.8 : The effect of column temperature on the shape of the peaks.

Open tubular columns, which are also known as capillary columns, come in two basic forms. The first is a wall-coated open tubular (WCOT) column and the second type is a support-coated open tubular (SCOT) column. While SCOT columns are capable of holding a greater volume of stationary phase than a WCOT column due to its greater sample capacity, WCOT columns still have greater column efficiencies.

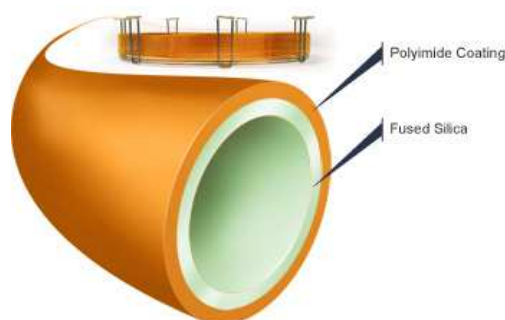


Figure 2.9 : Computer Generated Image of a FSWC column.

One of the most popular types of capillary columns is a special WCOT column called the fused-silica wall-coated (FSWC) open tubular column (see Fig. 2.9). The FSWC columns are commercially available and currently replacing older columns due to increased chemical inertness, greater column efficiency and smaller sampling size requirements [92].

The interface may serve only as a transfer line to carry the pressurized GC output into the evacuated ion source of the mass spectrometer. A jet separator interface can also serve as a sample concentrator by eliminating much of the carrier gas. It can permit carrier gas displacement by a second gas more compatible with the desired analysis, that is, carbon dioxide for chemically induced (CI) ionization for molecular weight analysis. It can be used to split the GC output into separate streams that can be sent to a secondary detector for simultaneous analysis by a completely different, complimentary method [91].

One of the most common types of mass analyzer in GC/MS is the quadrupole ion-trap analyzer, which allows gaseous anions or cations to be held for long periods of time by electric and magnetic fields. The mass spectrometer has three basic sections: an ionization chamber, the analyzer, and the ion detector (Fig. 2.10).

In the evacuated ionization chamber, the sample is bombarded with electrons or charged molecules to produce ionized sample molecules. These are swept into the high vacuum analyzer where they are focused electrically then selected in the quadrupole rods. The direct current (dc) signal charging apposing poles of the quadrupole rods creates a standing magnetic field in which the ions are aligned. Individual masses are selected from this field by sweeping it with a radio frequency (RF) signal. As different dc/RF frequencies are reached, different mass/charge ratio (m/z) ions are able to escape the analyzer and reach the ion detector. By sweeping from higher to lower frequency, the available range of m/z ions are released one at a time to the detector, producing a mass spectrum.

On entering the ion detector, the ions are deflected onto a cascade plate where the signal is multiplied and then sent to the data system as an ion current versus m/z versus time. The summed raw signal can be plotted against time as a total-ion chromatogram (TIC) or a single-ion m/z can be extracted and plotted against time as a single-ion chromatogram (SIC) [92].

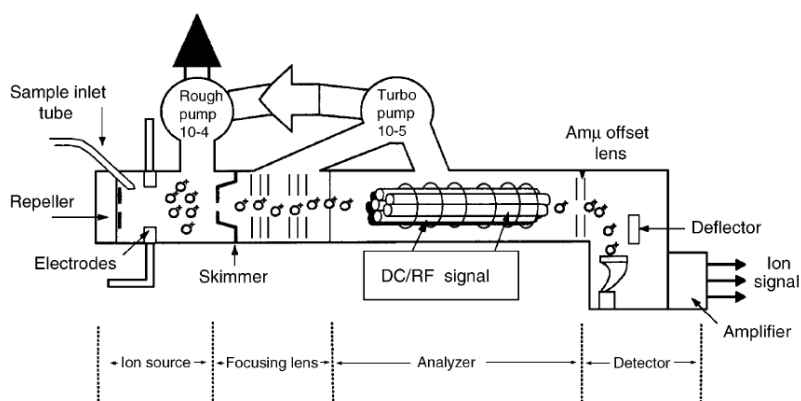


Figure 2.10 : Quadrupole mass spectrometer.

Unlike traditional GC detectors, a GC/MS system produces a 3-D data set. There are two basic operational modes:

- Scan - collect mass data over a known range. Maximum qualitative information.
- Selective Ion Monitoring (SIM) - sample at predetermined mass values. Maximum quantitative information.

Response/area information is obtained by summing spectra data for each scan. Scan data provides the maximum qualitative information. Available tools: Total ion chromatograms, extracted ion profile, mass spectra, library searches and creation.

A total ion chromatogram provides information similar to other GC detectors. Peak area is proportional to concentration (See Fig 2.11).

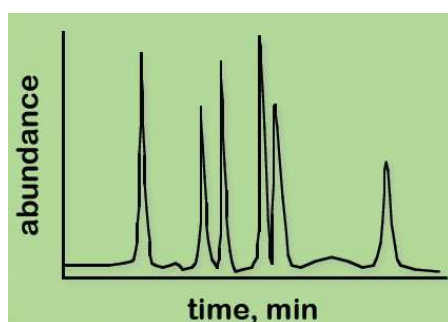


Figure 2.11 : Ion chromatogram.

Each point in a total ion chromatogram consists of an entire mass spectrum. Response for that point is determined by simply summing the abundances (See figure 2.12) [93].

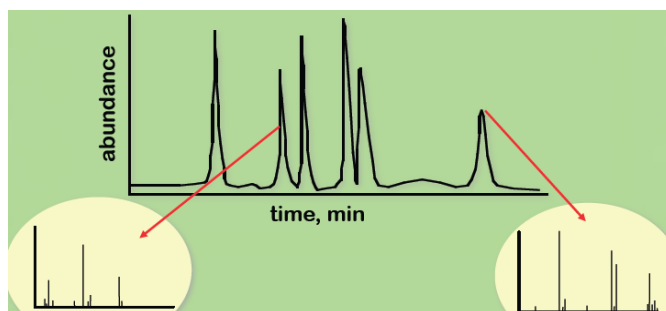


Figure 2.12 : Total ion chromatogram and mass spectrum.

2.5.2 Literature survey

This section summarizes results of some GC/MS phthalate testing studies in materials and products.

Phthalates were analysed with GC/MS also in air, wine, cow milk, drinking water, fatty food and cosmetic and personal care products in addition to PVC plastic products:

A gas chromatograph–mass spectrometry (GC–MS) method has been developed for the simultaneous determination of phthalate esters in clean room and indoor air in Hiroyuki Toda and his friend's study. Dibutyl phthalate (DBP), diethylhexyl phthalate (DEHP) present in air were collected using a Air cartridge and extracted with acetone and analysed by GC/MS. Analytical results for air samples collected from three office rooms ranged from 350 to 780 ngm^{-3} for dibutyl phthalate. However, the concentration of the determinants in four newly built clean rooms were under the minimum limits for determination of phthalate esters in air [94].

A method for the determination of six phthalate esters in wine samples has been developed by Michele Del Carlo et. al. The phthalates were extracted from wine samples with an optimised solid-phase extraction method and quantification was achieved via gas chromatography coupled with a mass spectrometer. A survey was performed on white and red wines from the market, winemakers and an experimental pilot plant. All the analysed samples were phthalate contaminated. Commercial wine showed higher detection frequency and level of total phthalate, DBP and BBP than those produced in a pilot plant. iBP and DEHP concentrations were similar in all the groups of samples. iBP concentration was higher in red wines than in white ones [95].

Phthalate esters released from plasticized polyvinyl chloride (PVC) tubing into raw cow milk during milking at dairy farms could be a potential source of contamination by phthalate esters in dairy products. A method was developed for the determination of these phthalate esters in raw cow milk samples using a headspace solid-phase microextraction (HS-SPME) technique by Yong-Lai Feng et. al. The milk samples were mixed with sodium chloride and extracted for 60 min at 90 °C. The phthalates collected on the SPME fibre were then desorbed in the GC injection port followed by GC-MS analysis in single ion monitoring (SIM) mode. This method was sufficiently sensitive to detect di-(2-ethylhexyl) phthalate, dibutyl phthalate (DBP) and diethyl phthalate (DEP) in two groups of raw cow milk samples. While similar levels were found in both types of samples for DBP and DEP, the level of DEHP was much higher in samples collected using PVC tubing (215.36 ng g⁻¹) than once without (16.04 ng g⁻¹), indicating potential leaching of DEHP from PVC tubing into raw cow milk [96].

Solid-phase microextraction (SPME) with an 85 mm polyacrylate fiber, coupled to gas chromatography–mass spectrometry was used to determine six phthalate esters and bis(2-ethylhexyl) adipate in water samples by A. Pen˜alver and his friends. The variables affecting the SPME absorption process were optimized and the method developed was applied to analyze both tap and commercial mineral water samples as well as water from the Ebro river and fishing and industrial ports. For real samples, the linear range in full scan acquisition mode was between 0.02 and 10 mg l for most compounds, and the limits of detection of the method were between 0.006 and 0.17 mg l [97].

In Ivan Ostrovsky and his friends' study new method for determination of total content of all phthalates in samples containing comparatively high fat fraction is presented. Method is based on phthalate hydrolysis to phthalic acid, selective removal of interfering lipophilic substances, esterification of phthalic acid to dimethyl phthalate and its GC-FID determination. Method was tested on 10 real samples of Baltic herring and codfish, butter, pork, goose and duck fats, sunflower, olive, rapeseed and linseed oils were analysed and the background corrected total phthalates content was found in the range from not detected level in duck fat to 12.5 µg g⁻¹ (nmol g⁻¹) in butter, respectively [98].

This study aims at determining phthalate levels in cosmetic and personal care products obtained from the Canadian market. Overall 252 products including 98 baby care products were collected at retail stores in several provinces across Canada in year 2007. These products included fragrances, hair care products (hair sprays, mousses, and gels), deodorants (including antiperspirants), nailpolishes, lotions (body lotions and body creams), skin cleansers, and baby products (oils, lotions, shampoos and diaper creams). Samples were extracted with different organic solvents, depending on the types of the products, followed by gaschromatography-massspectrometry (GC-MS) analysis. Of the 18 investigated phthalates, diethylphthalate(DEP), dimethylphthalate (DMP), diisobutylphthalate (DiBP), di-n-butylphthalate (DnBP) and di(2-ethylhexyl) phthalate (DEHP) were detected. The detection frequencies were in the following order: DEP (103 out of 252 products) > DnBP (15/252) > DiBP (9/252) > DEHP (8/252) > DMP (1/252). DEP was detected in almost all types of surveyed products with the highest levels (25.542 mg/g, equal to 2.6%) found in fragrances. DnBP was largely present in nail polish products with the highest concentration of 24.304 mg/g (2.4%). DnBP was also found in other products such as hair sprays, hair mousses, skin cleansers and baby shampoos at much lower concentrations (36 mg/g and less). Levels of other detected phthalates were generally low in the products [99].

Most important points of phthalate analysis are GC column selection, sample preparation, standard preparation and oven programming. This sections were explained in detail in for PVC products phthalate analysis studies below.

Yun Zou et. al. studied about the determination of common phthalates in plastic toys with different two methods. Their interested phthalates are:

- dibutyl phthalate (DBP)
- benzyl butyl phthalate (BBP)
- bis(2-ethylhexyl)phthalate (DEHP)
- di-n-octyl phthalate (DNOP)
- di-isononyl phthalate (DINP)
- di-isodecyl phthalate (DIDP)

Before testing, the samples (sample 1: PVC toy and sample 2: infant pacifier) were ground or cut into pieces sized at less than 3 mm × 3 mm. One gram of cut pieces

was Soxhlet extracted in dichloromethane, the extract was concentrated using a rotary evaporator and then diluted with DCM. The spiked samples were treated according to the GC/MS conditions described in Table 2.11 and Table 2.12.

Table 2. 11 : GC and MS conditions (Method GB/T 22048-2008-China Std).

| GC Conditions | |
|----------------------|---|
| Column | Agilent J&W DB-5ms Ultra Inert capillary column, 30 m × 0.25 mm, 0.25 μm (p/n 122-5532UI) |
| Inlet Temperature | Split @ 300 °C, split 20:1, split injection liner (Agilent p/n 5188-4647) |
| Carrier Gas | Helium, constant flow mode, 1.2 mL/min |
| Injection Volume | 1 μL, |
| Oven Program | 180 °C for 0.5 min; to 280 °C at 20 °C/min and hold for 7 min |
| MS Conditions | |
| Solvent Delay | 4.2 min |
| MS Temp | 230 °C (Source); 150 °C (Quad) |
| Transfer Line Tem. | 280 °C |
| MS | EI, SIM/Scan |
| Scan Mode | mass range (50-500 amu) |
| SIM Mode | ions |

Table 2. 12 : GC and MS conditions (CPSC Analytical Method).

| GC Conditions | |
|----------------------|--|
| Column | Agilent J&W DB-5ms Ultra Inert capillary column, 30 m × 0.25 mm, 0.25 μm (p/n 122-5532UI) |
| Inlet Temperature | 290 °C |
| Carrier Gas | Helium at 1 mL/min |
| Injection Mode | Splitless, pulse injection at 35 psi for 0.5 min, splitless injection liner (Agilent p/n 5188-3316). |
| Injection Volume | 1 μL |
| Oven Program | 50 °C for 1 min to 280 °C at 30 °C/min to 310 °C at 15 °C/min hold for 4 min |
| MS Conditions | |
| Solvent Delay | 5 min |
| MS Temp | 230 °C (Source); 150 °C (Quad) |
| Transfer Line Temp | 280 °C |
| MS | EI, SIM/Scan |
| Scan Mode | mass range (50-500 amu) |

The results for samples shown in Figure 2.13 and 2.14. In conclusion these methods have good linearity, repeatability, and recoveries for all target phthalate esters [100].

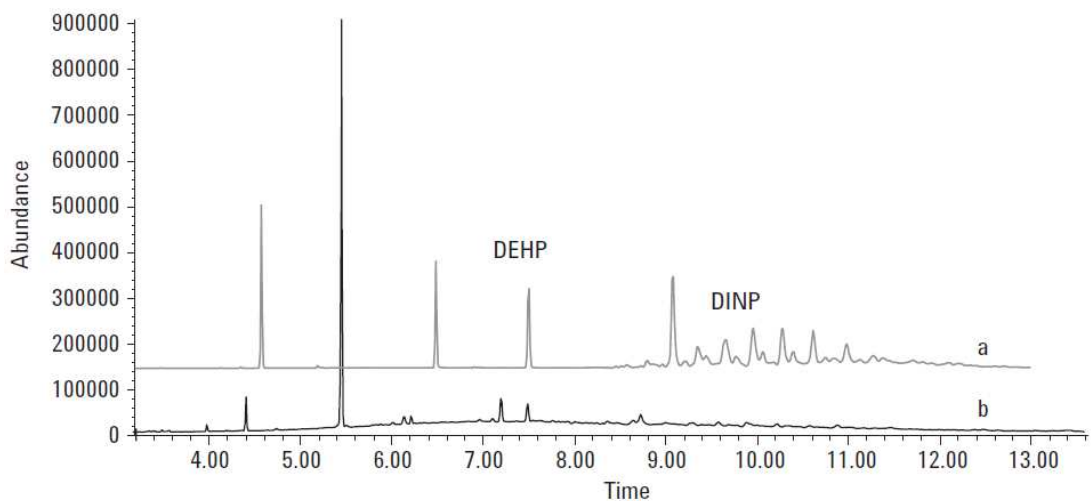


Figure 2.13 : Chromatographic results for the GC/MS analysis of one PVC toy sample (China Standard). (a) TIC of phthalates standards, (b) TIC of real sample.

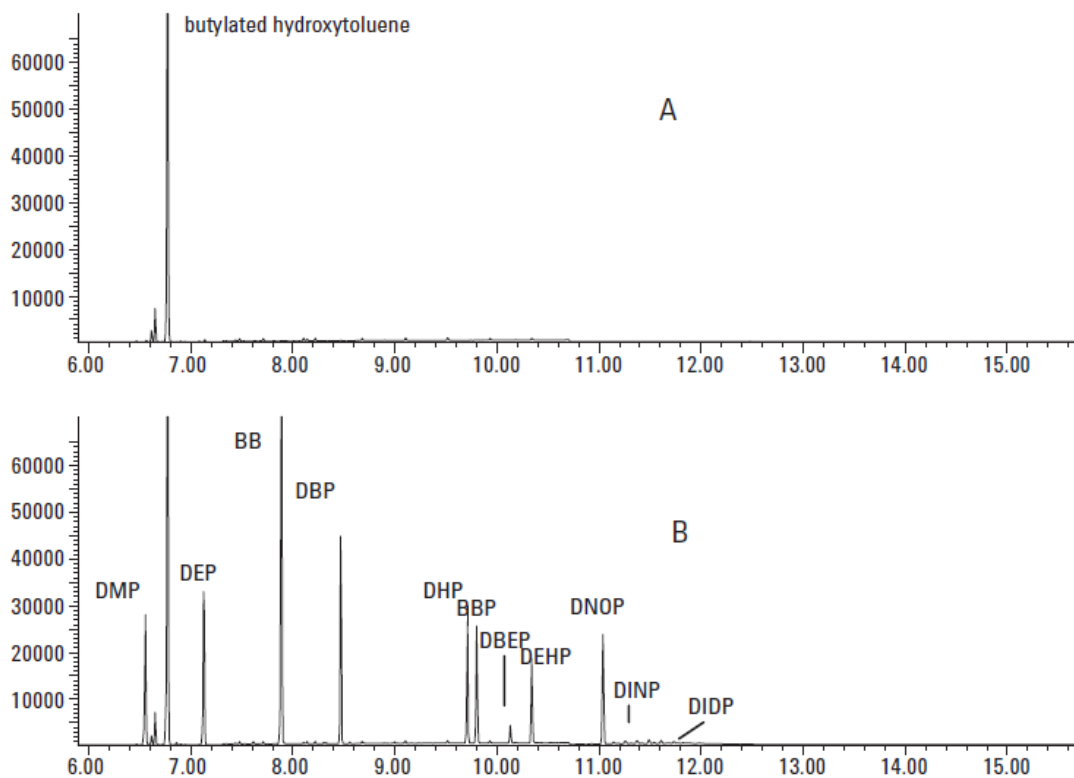


Figure 2.14 : TIC of infant pacifier extract (A) and sample 2 (pacifier) extract spiked with 2-ppm phthalate mixture (B). (CPSC Method).

Another study for phthalate analysis in children's products is done by W. Goodman. In this study the toy was cut into pieces 1 g in size. The extraction of phthalates from toy was assisted by sonication in methylene chloride. Following extraction, the

sample extract was filtered through a glass-fiber filter into an autosampler vial for analysis. The GC/MS conditions are given in Table 2.13.

Table 2. 13 : GC/MS Conditions.

| | | | |
|---|-------|---------------------|--|
| Gas Chromatograph: PerkinElmer Clarus 600 GC | | | |
| Analytical Column: Elite-5MS (30 m x .25 mm x 0.25 μ m) | | | |
| Injection Port Type: Programmable Split/Splitless | | | |
| Injector Temperature: 280 $^{\circ}$ C | | | |
| Injection Type: Split (25 mL/min) | | | |
| Syringe Volume: 5 μ L | | | |
| Injection Volume: 1 μ L | | | |
| Injection Speed: Normal | | | |
| Rinse Solvent: Methylene Chloride | | | |
| Carrier Gas Type: Helium | | | |
| Carrier Gas Program: Flow | | Hold Time | |
| 2 mL/min | | 0.5 min | |
| 1 mL/min | | Hold | |
| Oven Program: Temperature Hold Time Rate | | | |
| 100 $^{\circ}$ C | 0 min | 8 $^{\circ}$ C/min | |
| 260 $^{\circ}$ C | 0 min | 35 $^{\circ}$ C/min | |
| 320 $^{\circ}$ C | Hold | | |
| Instrument Timed Events: Split flow 50 mL/min @ 1 min | | | |
| Split flow 20 mL/min @ 5 min | | | |
| Mass Spectrometer: PerkinElmer Clarus 600 T MS | | | |
| GC Inlet Line Temp: 280 $^{\circ}$ C | | | |
| Ion Source Temp: 280 $^{\circ}$ C | | | |
| Function Type: Full Scan | | | |
| Full Scan Range: m/z 45-300 | | | |
| Full Scan Time: 0.15 sec | | | |
| InterScan Delay: 0.05 sec | | | |
| Solvent Delay: 3 min | | | |

A sample analysis is pictured in Figure 2.15; diisobutyl phthalate, and di-n-butyl phthalate are evident in chromatogram C. The total % weight of phthalates in this component was 0.007%.

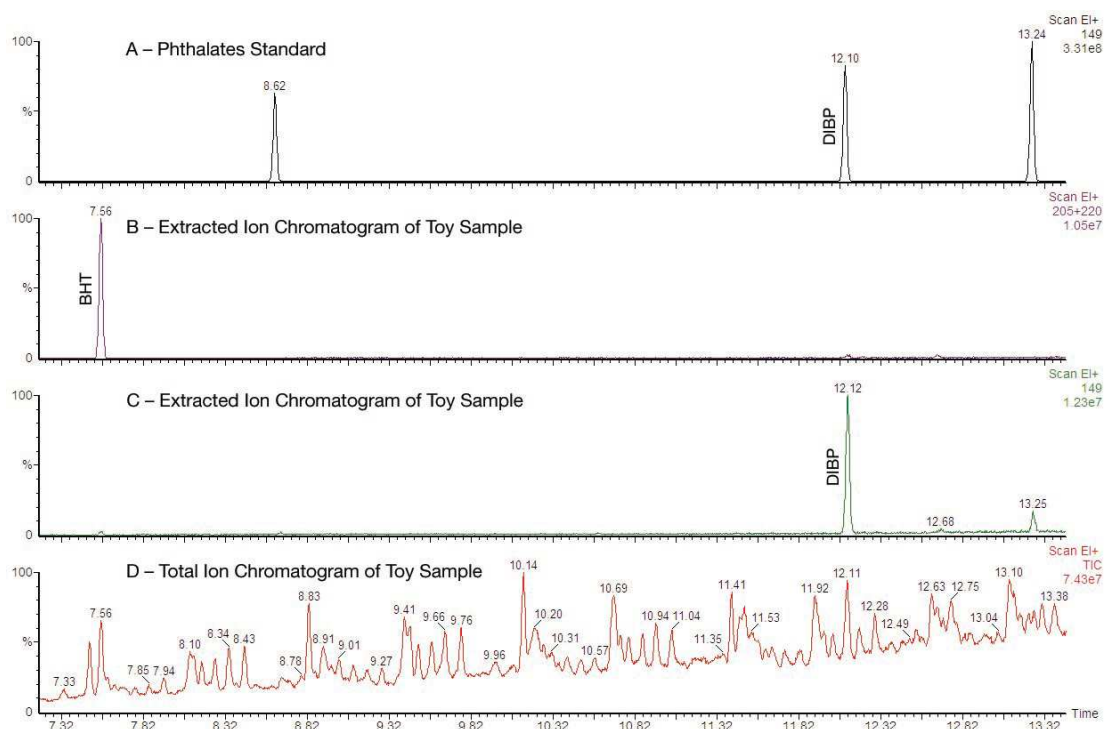


Figure 2.15 : Chromatograms of the analysis of a toy sample for phthalates.

Eventually the GC/MS analysis demonstrates separation and detection of common phthalates. This measurement achieved detection at levels considerably lower than the regulations [101].

In Q. Wang and his friend's study, separation methods of plasticizers in PVC tubes was carried out in different solvents and compared. 3 methods have been used. In method A, the tubes were cut into small pieces and dissolved in THF, then precipitated out by methanol. Dried extract was dissolved in chloroform and analysed by GC/MS; in method B1, small tube pieces soxhlet extracted in mixed solvent CCl_4/MeOH , in method B2 the tubes soxhlet extracted with EtO_2 and in method B3 the tubes extracted in CHCl_3 and the extracts were dissolved in chloroform and analysed by GC/MS, FTIR and TGA.

The extraction results for original tubes by different methods are summarized in Table 2.14. Comparison of the extracted additive concentration from different methods indicates that a big difference exists where methods B1 and B3 give higher concentrations, while methods A and B2 extracted lower amount of additive.

FTIR spectra (Fig. 2.16-17) of the remaining PVC from CHCl₃ of method B3 are similar to the pure PVC spectrum. When the remaining PVC was treated by method B3 again and dried under same conditions, the same weight was obtained, which indicates that no more plasticizer is retained in the remaining PVC.

Table 2. 14 : Separation of plasticizer from original tubes.

| Tube | Method | Original Weight (g) | Additive | | |
|----------|--------|---------------------|-----------------------------|------------------|------------------|
| | | | PVC ^a Extract | PVC ^b | PVC ^c |
| 1 | A | 0.6877 | 30.78 | 30.78 | - |
| | B1 | 0.7172 | 29.65 | | |
| | B2 | 0.3858 | 20.50 | 27.13 | 37.76 |
| | B3 | 0.2600 | 38.13 | | |
| | | | 25.71 | 27.16 | - |
| | | | 26.96 | | |
| 2 | A | 1.2539 | 34.99 | 34.99 | - |
| | B1 | 1.2443 | 33.34 | | |
| | B2 | 0.4686 | 17.86 | 24.80 | 36.26 |
| | B3 | 0.1216 | 37.81 | | |
| | | | 29.90 | 31.78 | - |
| | | | 30.52 | | |
| 3 | A | 0.7964 | 31.28 | 31.28 | - |
| | B1 | 0.7693 | 29.88 | | |
| | B2 | 0.5193 | 18.81 | 27.88 | 37.05 |
| | B3 | 0.2362 | 38.05 | | |
| | | | 23.76 | 25.59 | - |
| | | | 25.59 | | |
| | | 34.00 | 39.31 | 42.79 | |
| | | 41.19 | | | |

a The left PVC sample was dried at 80 °C for 30 min.

b The left PVC sample was further heated at 85 °C for 22 h.

c The weight loss of the left PVC at 200 °C from TGA analysis was taken into account.

TGA analysis showed 10 % weight loss of sample when heated at which temperature the pure PVC was stable under the same heating condition. These results confirm that residual solvent could not be thoroughly removed under the current heating condition and the remaining PVC was not thermally stable due to the loss of heat

stabilizer after extraction. On the other hand, when methanol was added to the dried extract to dissolve the plasticizer, a white solid precipitated out.

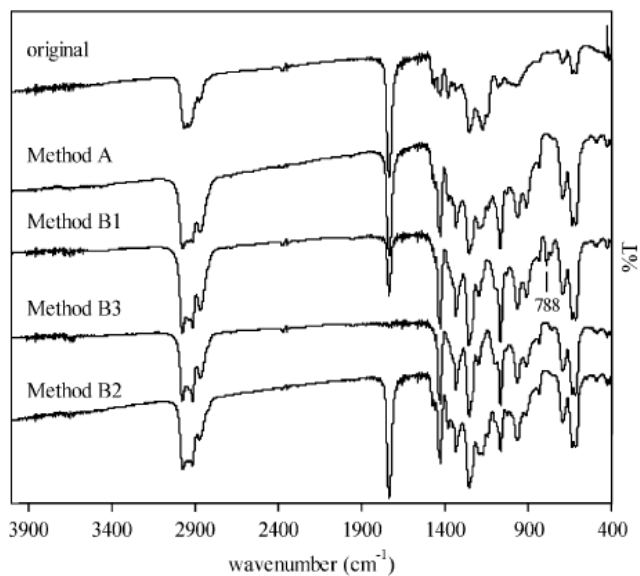


Figure 2.16 : The FTIR spectra of original tube 1 and the left PVC after different extractions.

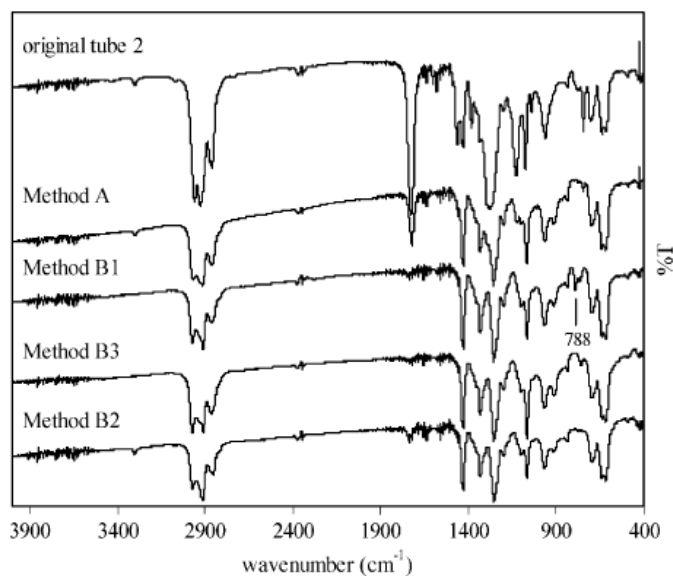


Figure 2.17 : The FTIR spectra of original tube 2 and the left PVC after different extractions.

The DSC analysis (Figure 2.18-19) on the original tubes and remaining PVC samples after extraction by different methods showed the changes in T_g and degradation temperature.

The small molecular weight plasticizers separated from the new tubes were identified by GC/MS and the results are listed in Table 2.15. Comparison of the plasticizer

separated by the four methods indicates that the extracts obtained from methods A and B2 contain antioxidant (butylated hydroxyl toluene, BHT), which was from the tubes because no BHT was found in the control experiment. No BHT can be found in the extract from methods B1 and B3.

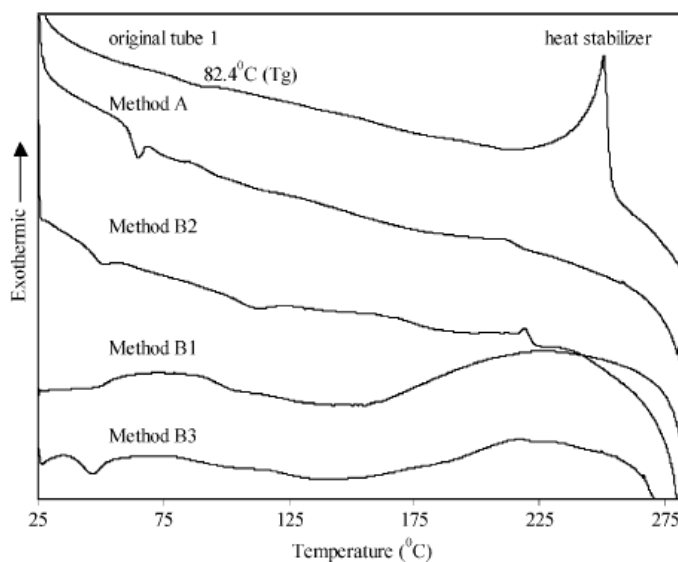


Figure 2.18 : The DSC curves of original tube 1 and the left PVC after different extractions.

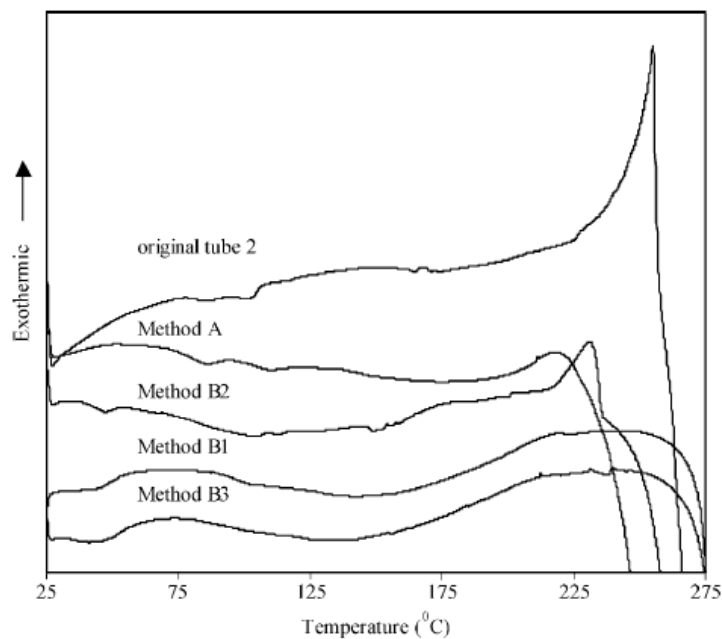


Figure 2.19 : The DSC curves of original tube 2 and the left PVC after different extractions.

Table 2.16 shows the DOP and DOA concentrations found in the three kinds of new tubes, where it can be seen that DOP was efficiently separated from the tubes by all

methods and close results were obtained, with an exception that relatively low DOP concentration was obtained from method A in tubes 1 and 3.

Table 2. 15 : Identification of extracted low molecular weight plasticizers by GC/MS analysis.

| Tube | Method A | Method B1 | Method B2 | Method B3 |
|----------|------------------------|---|------------------------|-------------------|
| 1 | BHT, HEA, DOA, IS, DOP | MPA, MOA, HAME, OAME, HEA, DOA, IS, DOP | BHT, HEA, DOA, IS, DOP | HEA, DOA, IS, DOP |
| 2 | BHT, IS, DOP | IS, DOP | BHT, IS, DOP | IS, DOP |
| 3 | BHT, HEA, DOA, IS, DOP | MPA, HAEM, MOA, HAME, OAME, HEA, DOA, IS, DOP | BHT, HEA, DOA, IS, DOP | HEA, DOA, IS, DOP |

BHT, butylated hydroxyl toluene; HEA, hexanedioic acid, mono(2-ethylhexyl) ester; DOA, bis (2-ethylhexyl) adipate; IS, di(cyclohexyl) phthalate; DOP, di(isooctyl) phthalate; MPA, methyl pentyl adipate; MOA, methyl 2-ethylhexyl adipate; HAME, hexadecanoic acid, methyl ester; OAME, octadecanoic acid, methyl ester; HAEM, hexanedioic acid, ethyl methyl ester.

Table 2. 16 : The amount (wt%) of extracted DOP and DOA determined by GC analysis.

| Tube | Plasticizer | Method A | Method B1 | Method B2 | Method B3 |
|----------|------------------|----------|-----------|-----------|-----------|
| 1 | DOA ^a | 0.47 | 0.39 | 0.49 | 0.48 |
| | DOP ^a | 0.025 | 0.03 | 0.027 | 0.028 |
| | DOA ^b | 0.41 | 0.36 | | |
| | DOP ^b | 3.27 | 3.12 | | |
| 2 | DOP | 28.52 | 28.73 | 29.51 | 29.15 |
| 3 | DOA | 0.52 | 0.49 | 0.50 | 0.52 |
| | DOP | 0.051 | 0.060 | 0.057 | 0.056 |

^a The new tube 1 product.

^b The old tube 1 product.

In conclusion, the separation and analysis of plasticizer in three kinds of PVC tubes by different methods were investigated. It was found that both low and high molecular weight plasticizers co-precipitated with PVC in the dissolve/precipitation (THF/MeOH) process. Some polyadipates retained in PVC after Soxhlet extraction in Et₂O. Degradation of additives occurred during the extraction in the mixed solvent (CCl₄/ MeOH). The simple chloroform room temperature extraction was found to be

the most efficient method where plasticizer and heat stabilizer were well extracted from PVC. Analysis on one kind of the used tubes showed that 64-67% of DOP migrated to the service environment, while 70–100% DOA was retained [102].

The migration of phthalates into saliva was also studied by A. O. Earls et. al. Two migration methods used.

1- Simulated method: PVC samples and saliva simulant were agitated in a shaking waterbath (glass balls added for submersion of sample), then extracted with dichloromethane and added to n-hexane.

2- Stringent method: Same with simulated method except the saliva temperature (higher temperature) and in this method stainless steel balls used.

The results are shown in Table 2.17-28. The study represented, stringent method is most suitable for the assesment of toy and childcare articles intended to be mouthed [103].

Table 2. 17 : Migration test results—Simulated method.

| | Mean (%) |
|--|-------------------|
| <i>Solution tested</i> | |
| DINP recovery (200 µg/ml) | 90.0 |
| DIDP recovery (200 µg/ml) | 87.1 |
| DEHP recovery (10 µg/ml) | 86.4 |
| <i>Repeatability and reproducibility of PVC disc</i> | |
| DINP PVC reference disc | 1.43 ^a |
| <i>Phthalate release from test samples</i> | |
| DINP-fruit teether | 0.7 ^a |
| DIDP-bath animal | 1.2 ^a |
| DEHP-high chair | 1.6 ^a |
| DEHP swimming armband | 1.2 ^a |

Recovery solutions were prepared in propan-2-ol, diluted in saliva simulant solution and extracted with dichloromethane. The extract was finally prepared in n-hexane for GC–MS analysis.

^a µg/10 cm² /min.

Determination of eight phthalates in plastic products for food use with GC/MS is reported in H. Y. Shen's study. Polyethylene packaging bags, previously shown to be

free from target compounds, were spiked with each of phthalates and used as spiked samples.

Table 2. 18 : Migration test results—Stringent method.

| | Mean (%) |
|--|------------------|
| <i>Solution tested</i> | |
| DINP recovery (200 µg/ml) | 89.9 |
| DIDP recovery (200 µg/ml) | 88.0 |
| DEHP recovery (10 µg/ml) | 88.0 |
| <i>Repeatability and reproducibility of PVC disc</i> | |
| DINP PVC reference disc | 8.8 ^a |
| <i>Phthalate release from test samples</i> | |
| DINP-fruit teether | 5.0 ^a |
| DIDP-bath animal | 3.9 ^a |
| DEHP-high chair | 4.1 ^a |
| DEHP swimming armband | 3.1 ^a |

See Table 7.9 for experimental detail.

^a µg/10 cm² /min.

The optimization of extraction efficiency was performed with varying extractants: hexane, acetone or water. Homogenization, ultrasonication or shaker was taken as the second factor from optimizing of phthalates isolation from matrices.

The GC/MS parameters shown in Table 2.19. The results of the experiments of spiked polyethylene packaging bag were shown in Table 2.20.

As a result, it was found that phthalates could be efficiently extracted by sonication-assisted solvent extraction system after sample treatment with liquid nitrogen [104].

C. George suggested a new analytical method of detecting and characterizing phthalate esters which is applicable to a wide variety of matrices. In this study methane and ammonia as a reagent gas and ionization types (PCI and EI) were compared.

As shown in EI mass spectrum (Figure 2.20), GC provides some separation of the phthalates but with the array of possible isomers and essentially a single identifying ion, distinguishing the individual phthalates of concern is difficult.

Table 2. 19 : Gas chromatographic and mass spectrometric parameters used for analysis of phthalates in selected plastic products used in food packing, storage and in utensil.

| Parameter | |
|---|--|
| Injector (splitless mode) temperature (°C): | 250 |
| Injection volume (µL) | 1.0 |
| GC temperature program | 150 °C (hold 0.5 min) 220 °C (5.0 °C/min) 275 °C (3.0 °C/min, hold 13 min) |
| GC carrier gas: | He (mL/min) 1.0 |
| Aux (°C) | 280 |

EI

| | |
|-------------------------------------|------|
| Ion source (°C) | 230 |
| Quadrupole (°C) | 150 |
| Electron energy (eV) | 70 |
| Ionisation current (mA) | 34.6 |
| Electronic multiplier potential (V) | 1200 |

Table 2. 20 : Effects of isolation approaches and extractants on extraction of phthalates in selected plastic products used in food packing, storage and in utensil spiked packaging bag of DEP (100.0 ug/kg) determined by GC–MS–SIM.

| Entry | Isolation | Extractant | DEP (found µg/kg) |
|--------------|------------------|-------------------|--------------------------|
| 1 | Homogenisation | Hexane | 86.2 |
| 2 | | Acetone | 76.8 |
| 3 | | Water | 68.5 |
| 4 | Ultrasonication | Hexane | 90.5 |
| 5 | | Acetone | 126.2 |
| 6 | | Water | 78.5 |
| 7 | Shaker | Hexane | 83.1 |
| 8 | | Acetone | 113.2 |
| 9 | | Water | 75.6 |

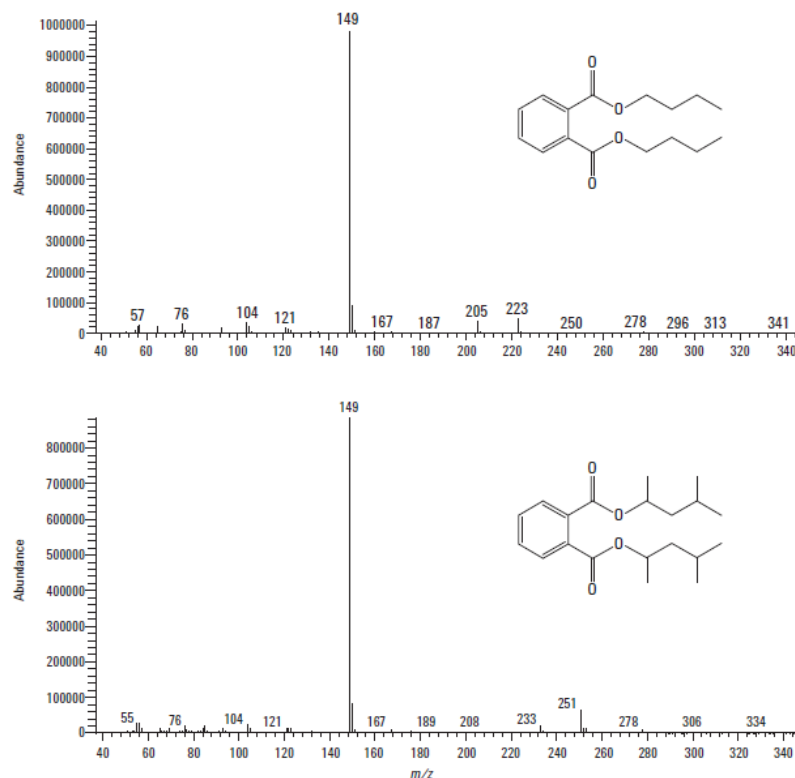


Figure 2.20 : Electron impact ionization mass spectra of di-n-butyl phthalate (upper panel) and bis(4-methyl-2-pentyl) phthalate (lower panel) from m/z 50 to 350 at 70 eV. Notice the lack of intense fragments and molecular ions. The molecular weights are 278 and 334 g/mole, respectively.

Although positive chemical ionization (PCI) with methane provides more information than EI on phthalate identity, the methane reagent is still rather unselective in ionization and produce more chemical noise in the background. Applying ammonia as the reagent gas in PCI to reduce chemical noise and enhance identification of the phthalates is more useful approach. When combined with retention time locking, identification of phthalates becomes more simplified. See Figure 2.21 for comparing the spectra using methane versus ammonia as a reagent gas.

As conclusion, it was found that, combination of positive chemical ionization with retention time locking and using ammonia as a reagent gas would be suitable for use in phthalate determinations in environmental media, plastics, cosmetics and many other matrices [105].

Another study was done by Ting Wu and his friends which discussed a new UPLC and HPLC methods used for phthalate analysis. According to the results of the study it was found that UPLC's advantages were speed, resolution and sensitivity compared to HPLC. The main advantage was a particularly substantial reduction of analysis time, which also meant reduces solvent consumption. And also it was found that the sensitivity of UPLC was much higher than that of a conventional HPLC. But a negative aspect of UPLC could be the higher back pressure than in conventional HPLC [89].

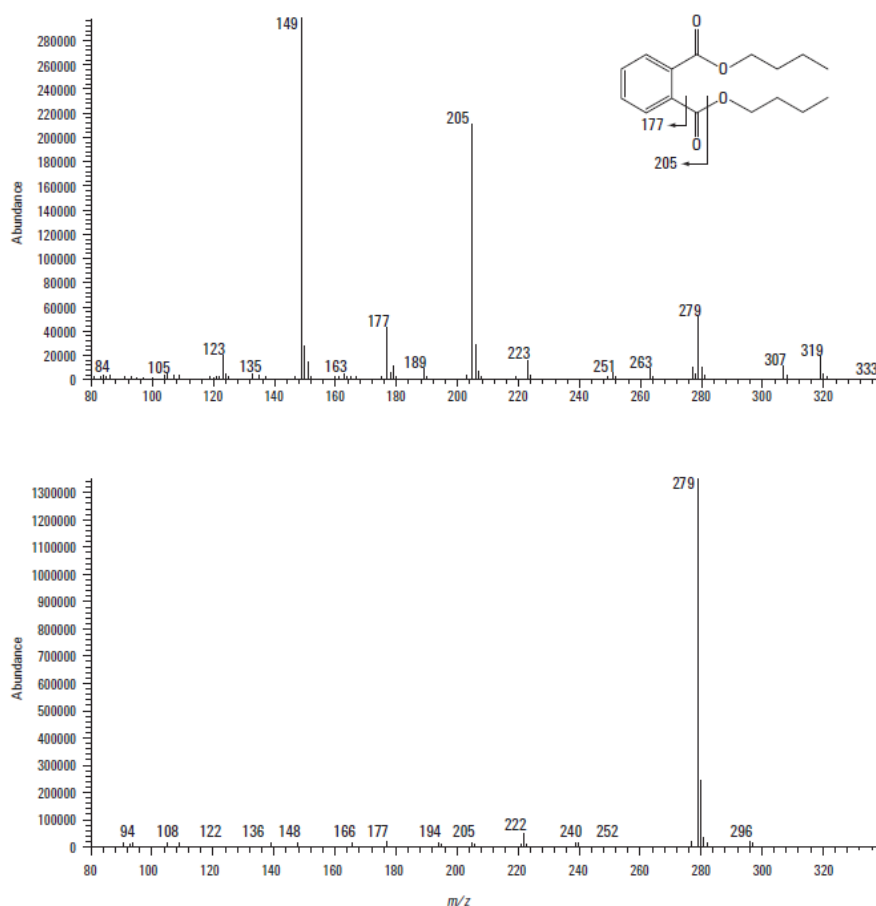


Figure 2.21 : PCI methane (upper panel) and ammonia (lower panel) mass spectra of di-n-butyl phthalate. The PCI methane mass spectrum shows substantial fragmentation but relative to the EI spectrum in Figure 2.20, high abundance for the higher m/z ions such as the protonated molecule at m/z 279. The ion at m/z 205 is generated by loss of an oxybutyl fragment. The PCI-ammonia mass spectrum consists almost completely of the protonated molecule.

3. EXPERIMENTAL

3.1 Chemicals Used

3.1.1 Phthalic acid, bis-2-ethylhexyl ester (DEHP)

Phthalic acid, bis-2-ethylhexyl ester (DEHP) was obtained from Dr. Ehrenstorfer GmbH. It was used as standard and its concentration was 98.5%.

3.1.2 Phthalic acid, bis-butyl ester (DBP)

Phthalic acid, bis-butyl ester (DBP) was obtained from Dr. Ehrenstorfer GmbH. It was used as standard and its concentration was 99%.

3.1.3 Phthalic acid, benzylbutyl ester (BBP)

Phthalic acid, benzylbutyl ester (BBP) was obtained from Dr. Ehrenstorfer GmbH. It was used as standard and its concentration was 99.5%.

3.1.4 Phthalic acid, bis-iso-nonyl ester (DINP)

Phthalic acid, bis-iso-nonyl ester (DINP) was obtained from Dr. Ehrenstorfer GmbH. It was used as standard and its concentration was 98.5%.

3.1.5 Phthalic acid, bis-n-octyl ester (DNOP)

Phthalic acid, bis-n-octyl ester (DNOP) was obtained from Dr. Ehrenstorfer GmbH. It was used as standard and its concentration was 99.5%.

3.1.6 Phthalic acid, bis-iso-decyl ester (DIDP)

Phthalic acid, bis-iso-decyl ester (DIDP) was obtained from Dr. Ehrenstorfer GmbH. It was used as standard and its concentration was 99.5%.

3.1.7 Phthalic acid, bis-iso-butyl ester (DIBP)

Phthalic acid, bis-iso-butyl ester (DIBP) was obtained from Dr. Ehrenstorfer GmbH. It was used as standard and its concentration was 99.5%.

3.1.8 Benzoic acid-benzyl ester (BB)

Benzoic acid-benzyl ester was obtained from Dr. Ehrenstorfer GmbH. It was used as internal standard and its concentration was 99.5%.

3.1.9 n-Hexane

n-Hexane was obtained from Merck. It was used as solvent and its concentration was 95%.

3.1.10 Methanol

Methanol was obtained from Merck. It was used as solvent and its concentration was 99.9%.

3.1.11 Chloroform

Chloroform was obtained from Merck. It was used as solvent and its concentration was 99.9%.

3.2 Equipment Used

3.2.1 Microwave Accelerated Reaction System

CEM Mars 5 model Microwave Accelerated Reaction System was used for extraction of phthalates from the samples.

3.3.2 Soxhlet extractor

Soxhlet Extractor was used in the extraction of phthalates from the samples.

3.3.3 Rotary evaporator

IKA HB 10 BASIC model rotary evaporator was used for evaporating the chloroform and methanol from the extract solution.

3.3.4 Infrared spectrophotometer (FT-IR)

IR Prestige-21 model Infrared spectrophotometer (FT-IR) was used for obtaining the IR-Spectra of the samples.

3.2.5 Gas chromatography - mass spectroscopy (GC-MS)

Agilent 7890A GC System and Agilent 5975C VL MSD were used for analysis of phthalates contained in the samples.

3.3 Experimental Procedure

3.3.1 Preparation of reagents (standard solutions)

A mix solution were prepared from 1000 ppm individual stock phthalate ester solutions. 100 µl from each DEHP, BBP, DBP, DIBP stocks and 1000 µl from each DIDP and DINP solutions were taken into a 10 ml volumetric flask and filled with n-hexane to 10 ml. This solution was called 10/100 ppm mix standard.

The 0.2; 0.5; 1; 2; 5 ppm calibration solutions were prepared into vials using the 10/100 ppm mix standard according to Table 3.1.

Table 3. 1 : Preparation of calibration standard solutions.

| Concent. (ppm) | n-Hexane (µl) | Mix Std. (µl) | IS (BB) (µl) |
|----------------|---------------|---------------|--------------|
| 0.2 | 980 | 20 | 10 |
| 0.5 | 950 | 50 | 10 |
| 1 | 900 | 100 | 10 |
| 2 | 800 | 200 | 10 |
| 5 | 500 | 500 | 10 |

3.3.2 Preparation of samples

The following samples (shown in Figure 3.1) were chosen from a washing machine to analyse the phthalate content:

1. Black hose
2. Grey hose
3. Bellow
4. Vent hose
5. Gasket
6. Cable

Two methods were used for extraction of phthalate esters from the samples:

In microwave extraction method - The samples were cut into small pieces (weighed around 0.5 g). Because grinding the sample into a very small particle size, increasing its surface area, will improve the extraction efficiency.

The each small sample pieces were put into separate explosion proof reaction vessels (shown in Figure 3.2) and 6 ml chloroform and 3 ml methanol were added. First vessel was blank and only contained methanol and chloroform. Each seven vessels were put into the vessel module and placed into the microwave oven. Microwave condition is shown in Table 3.2.



Figure 3.1 : Tested samples.



Figure 3.2 : Reaction vessels.

Table 3. 2 : Microwave oven conditions.

| Power | Ramp | PSI | °C | Hold |
|--------------|-------------|------------|-----------|-------------|
| 100% | 10:00 | 200 | 80 | 20:00 |



Figure 3. 3 : Microwave oven.

After the microwave extraction, the extracts were filtered with a filter paper to the 100 ml volumetric flasks; chloroform and methanol were evaporated with rotary evaporator (shown in Figure 3.4) at 80 °C for 5 mins.

Evaporated samples were filtered with a glass wool in 25 ml volumetric flasks. 15 ml n-hexane added to the flask and cured in ultrasonic sonicator for 2-3 seconds.

After curing solutions were filtered with glass wool again (shown in Figure 3.5) to the 25 ml volumetric flasks and filled with n-hexane.



Figure 3.4 : Rotary evaporator.



Figure 3.5 : Glass wool filtration.

Finally 1 ml of each samples were taken to the and 10 μ l IS were added capped vials for GC-MS analysis.

In soxhlet extraction method - Soxhlet extraction was used (shown in Figure 3.6) for only cable sample. The sample were placed in pre-weighed 150 ml flat bottomed flask and heated in oven at $(105 \pm 5) ^\circ\text{C}$ for (30 ± 5) min. Cooled in desiccator. Then the flask and sample were weighed together.



Figure 3.6 : Soxhlet extractor.

The sample were cut into small pieces ($< 5 \text{ mm } \Phi$), then weighed (2 ± 0.2) g of the pieces into Soxhlet thimble and cotton wool was added to the top of the thimble.

(50 ± 10) ml of diethyl ether was added into the flask, refluxed gently for $6 \text{ h } \pm 30$ min, then cooled in desiccator. The diethyl ether was completely evaporated by means of steam bath. The flask was placed in oven at $(105 \pm 5) ^\circ\text{C}$ for (30 ± 5) min. and cooled. Drying and cooling cycles were repeated until the difference between two consecutive weighings were not more than 0.0005 g. A blank solution were run consecutively.

(50 ± 2) ml of n-Hexane was added to the weighed extract. The flask was stoppered and swirled to completely dissolve the extract. The solution was decanted into a 200 ml volumetric flask, repeatedly rinsing the flask with n-hexane. And a portion of the solution were transferred to the capped vial with adding 10 μl IS for GC-MS analysis.

3.4 Tests and Analysis

3.4.1 FT-IR analysis

A IR Prestige-21 Infrared spectrophotometer was used to obtain all infrared spectra of the samples. IR spectra obtained from solid samples for analysing of the chemical structure and material type of six samples. Spectra were recorded at 4 cm^{-1} resolution by averaging 10 scans.

FTIR bands of PVC, elastomers, PE and polyamides are as follows:

In the measurement of the soft PVC, the peaks in the vicinities of 1425 cm^{-1} , 959 cm^{-1} and 610 cm^{-1} are peaks originating from the PVC. Therefore, in many infrared spectra of soft PVC, verification of PVC is accomplished using the C – Cl stretching vibration near 610 cm^{-1} [106].

Structure of polyethylene or is composed almost completely of methylene groups ($-\text{CH}_2$). its infrared spectrum would be expected to consist solely of methylene stretches and bends. Four sharp peaks dominate the spectrum: The methylene stretches at $2,920$ and $2,850\text{ cm}^{-1}$ and the methylene deformations at $1,464$ and 719 cm^{-1} . Due to the crystallinity of polyethylene, the $1,464$ and 719 cm^{-1} peaks are split, and additional peaks are seen at $1,473$ and 731 cm^{-1} .

An elastomer can be made from the copolymerization of ethylene and propylene. The ethylene content of EP rubber usually ranges from 50 to 75%. A diene is regularly added to provide sites for crosslinking. The diene content in EPDM is customarily less than 10%, and infrared peaks due to this component are thus very weak. The spectrum is dominated by the methylene peaks at $2,925$, $2,854$, $1,464$ and 721 cm^{-1} . The methyl ($-\text{CH}_3$) peak at $1,377\text{ cm}^{-1}$ is also significant. The methyl stretches can be seen as shoulders at $2,952$ and $2,871\text{ cm}^{-1}$.

Polyamides, better known as nylons, are made from the polymerization of lactams or the condensation of diamines with dicarboxylic acids. The number following the name, e.g., nylon 6 or nylon 6,6, indicates the number of carbon atoms in the starting material(s). The strongest peaks are those of the Amide I and Amide II bands found near $1,640$ and $1,545\text{ cm}^{-1}$, respectively. Also, the N-H stretch near $3,300\text{ cm}^{-1}$ is very intense. Different nylons can be distinguished by subtle differences in frequencies and intensities in the Amide III band between $1,260$ and $1,280\text{ cm}^{-1}$, and in the symmetric methylene stretch and the methylene deformation bands [107].

Typical infrared spectrums of DEHP, DBP, BBP, DIBP (phthalates in the SVHC list) are also shown in Figure 3.7-10 [108-111].

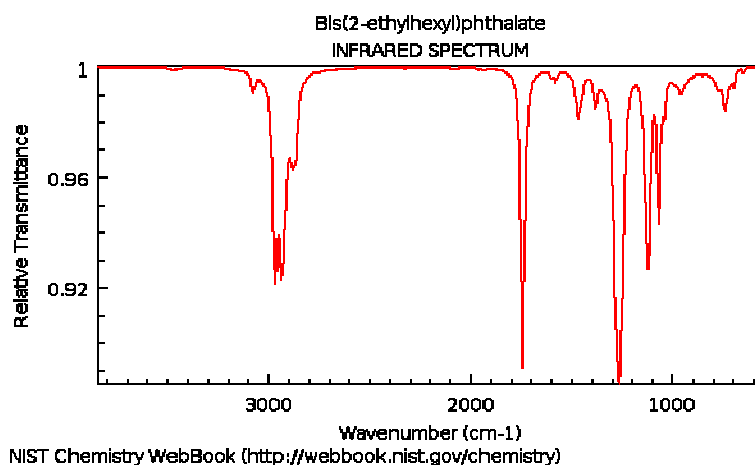


Figure 3.7 : IR Spectrum of DEHP

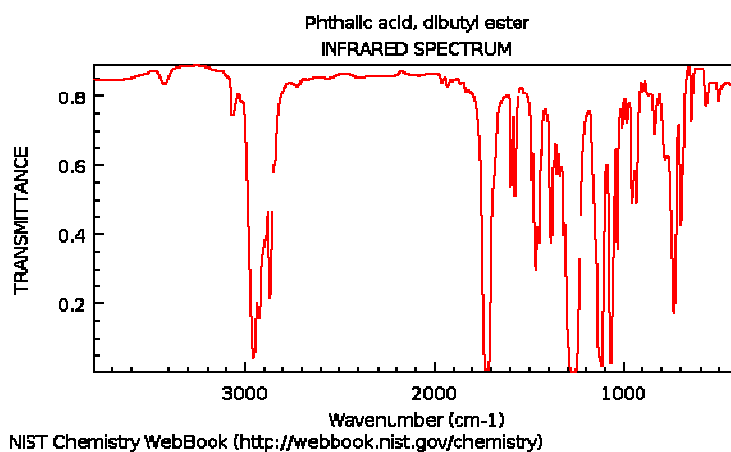


Figure 3.8 : IR Spectrum of DBP

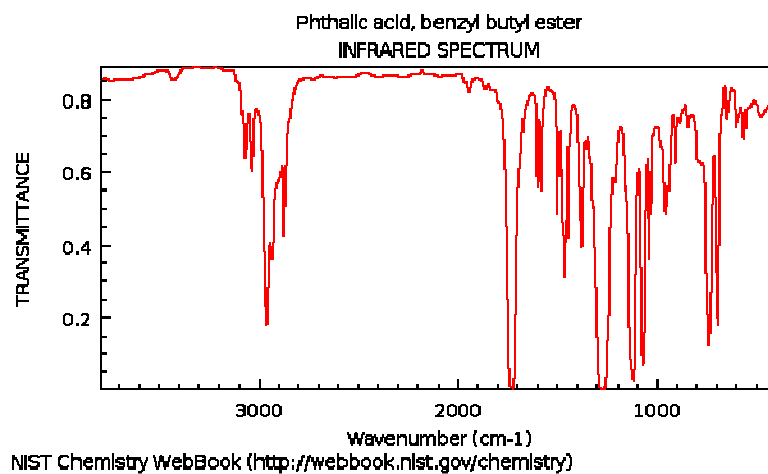


Figure 3.9 : IR Spectrum of BBP

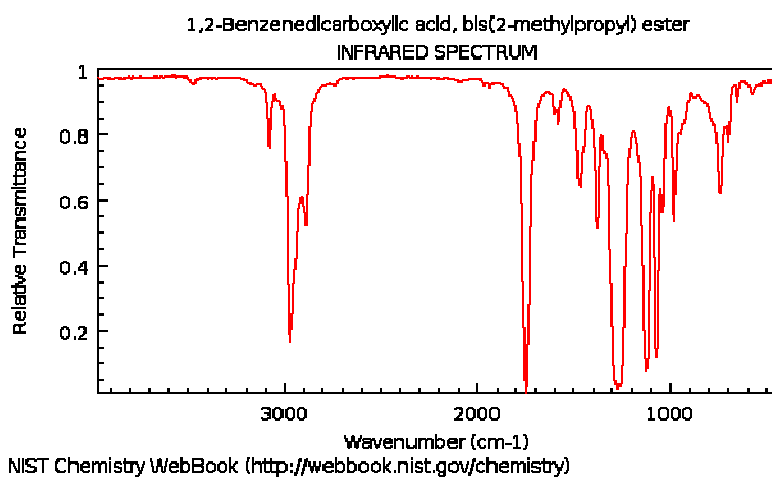


Figure 3. 10 : IR Spectrum of DIBP

3.4.2 GC-MS analysis

GC-MS analysis was performed with Agilent 7890A GC System Agilent 5975C VL MSD GC/MS system.

Prepared standard solutions and samples were tested respectively:

- 1- Blank
- 2- Standards
- 3- Sample blank
- 4- Samples

GC-MS parameters are shown in Table 3.3. GC-MS spectra of mix standard solution (0.5 ppm) is also shown in Figure 3.11.

Table 3. 3 : GC-MS conditions.

| GC Parameters |
|---|
| Analytical column: HP-5MS (30m x 250 μ m x 0.25 μ m) |
| Injection type: pulsed splitless (34 ml/min) |
| Injection temperature: 290 °C |
| Syringe volume: 1 μ l |
| Injection volume: 1 μ l |
| Injection dispense speed: 6000 μ l/min |
| Carrier gas type: Helium |
| Oven program: 50 °C for 1 min then 30 °C/min to 280 °C for 0 min then 15 °C/min to 310 °C for 4 min |
| MS Parameters |
| Solvent delay: 5 min |
| MS Temp: 230 °C (source); 150 °C (quad) |
| SIM mode: Ions |

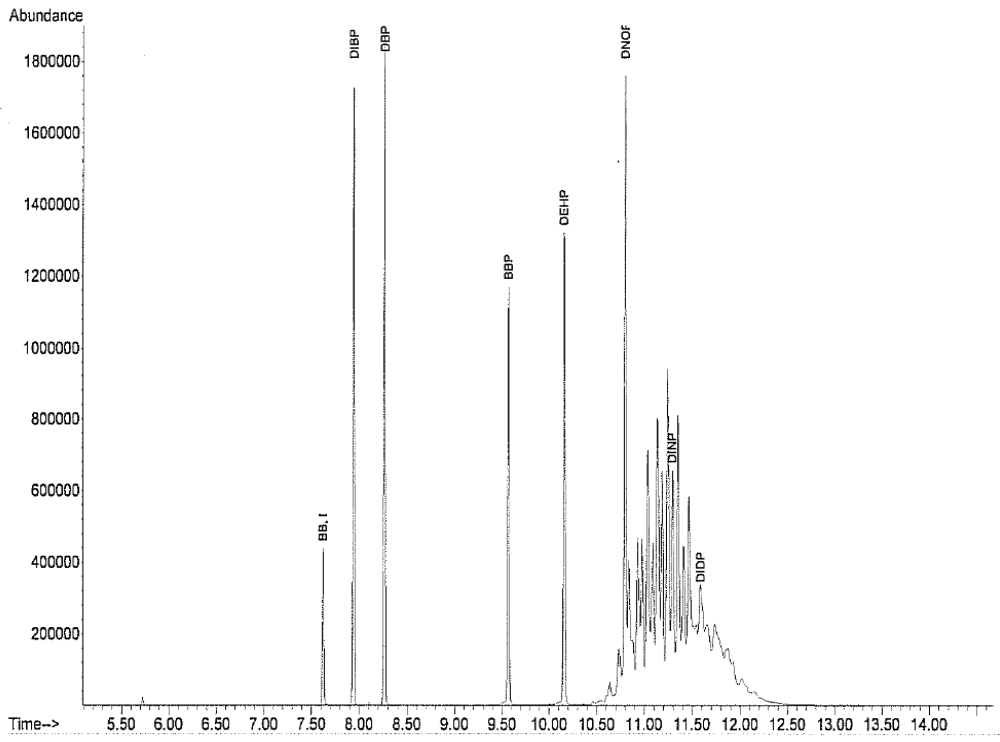


Figure 3. 11: GC-MS spectra of mix standard solution (0.5 ppm).

4. RESULTS AND DISCUSSIONS

In this study 6 samples were selected various polymeric materials from a washing machine. This 6 samples were characterized by FTIR analysis. Samples were prepared according to methods specified in section 3.3.2 for identifying the content of DIBP, DBP, BBP, DEHP, DNOP, DINP, DIDP phthalates. Calibration curves were plotted with GC-MS method for analysing the phthalates. Thus in this study quantitative analysis of 7 types of phthalates in 6 various samples have been done.

Calibration graphs were plotted with response against the known standard concentrations shown in Figure 4.1-4.7.

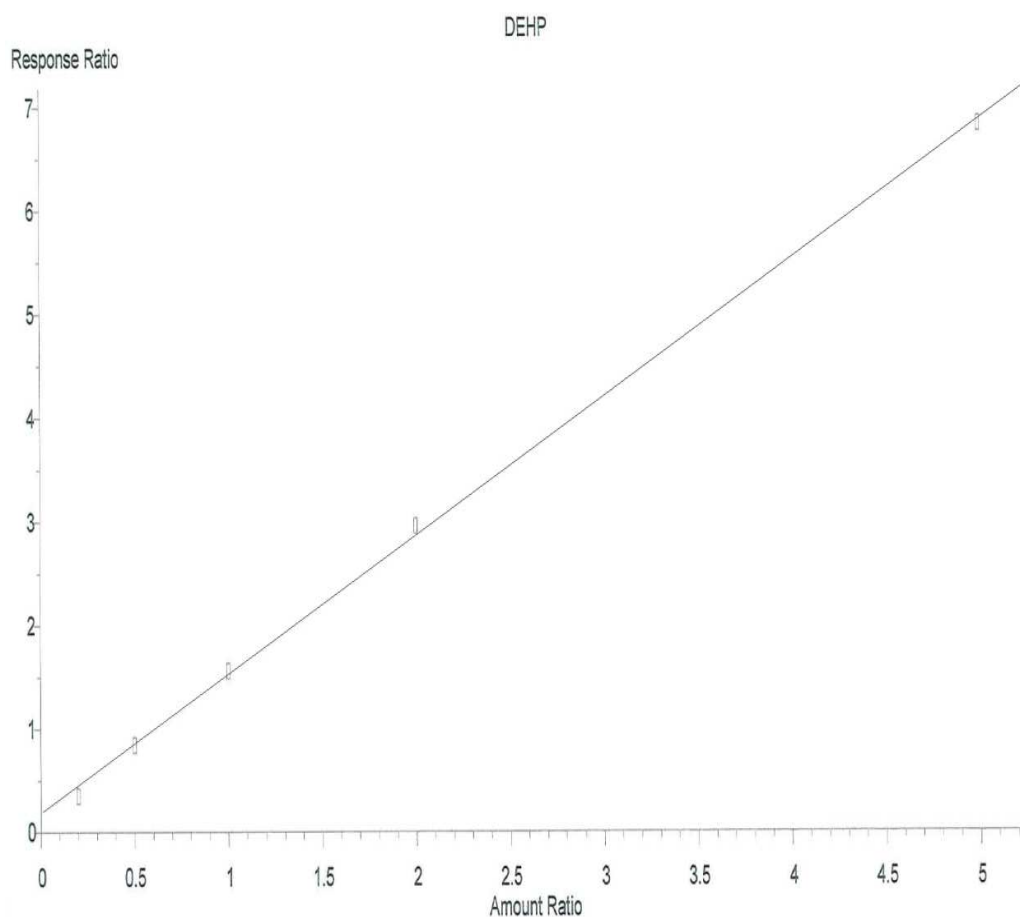


Figure 4. 1 : Calibration data of DEHP.

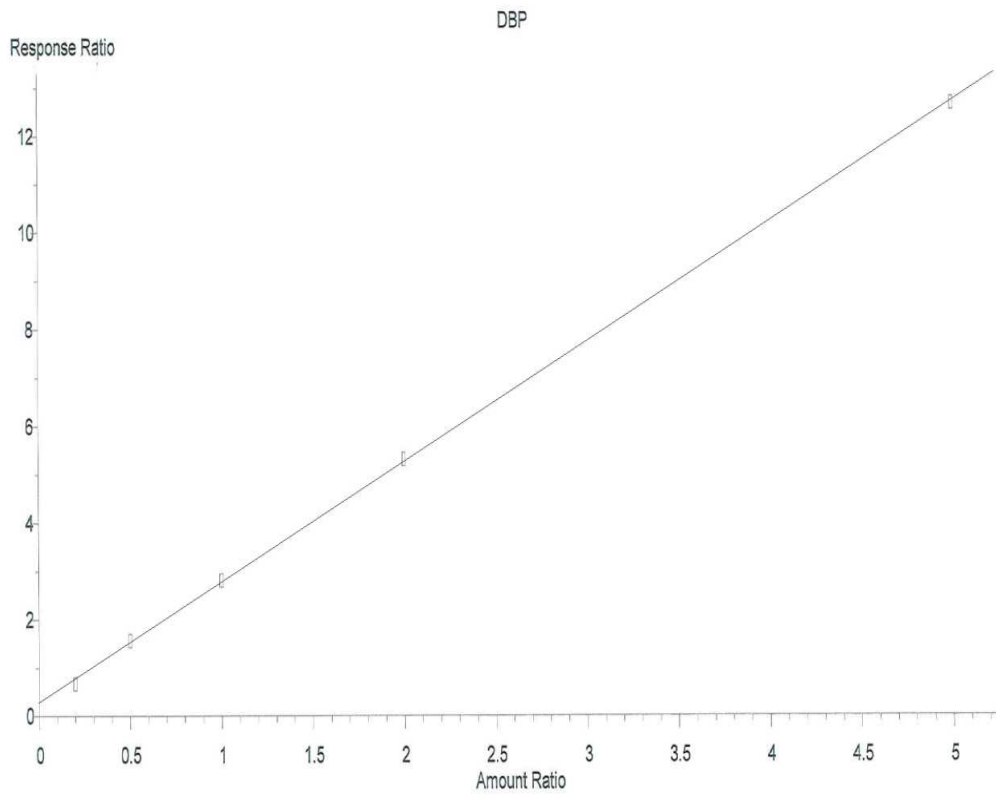


Figure 4.2 : Calibration data of DBP.

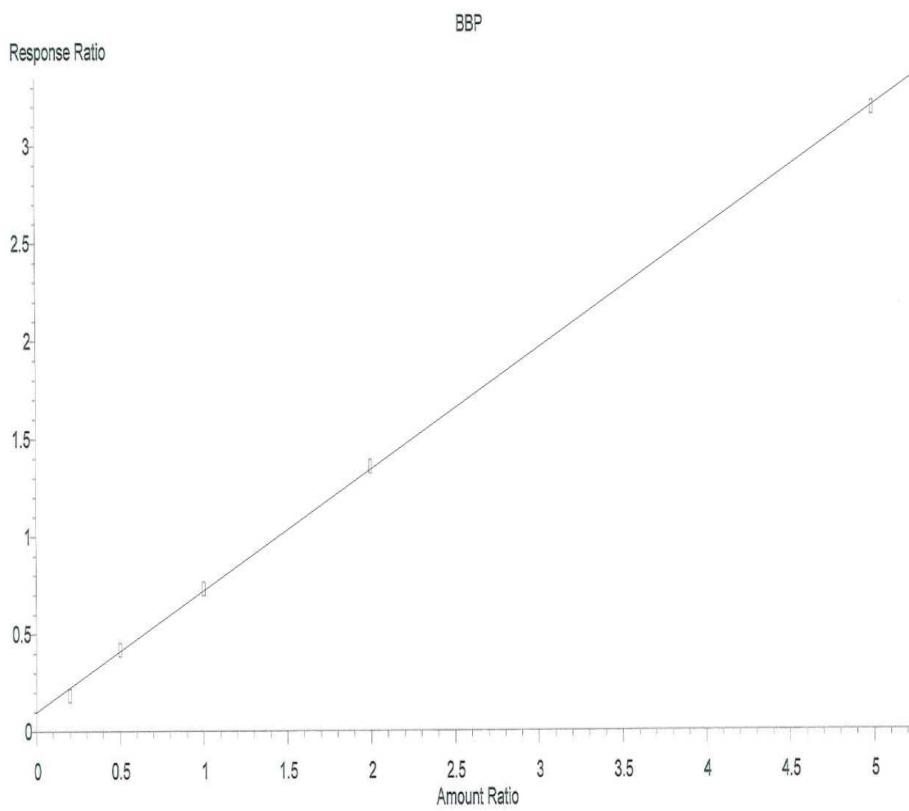


Figure 4.3 : Calibration data of BBP.

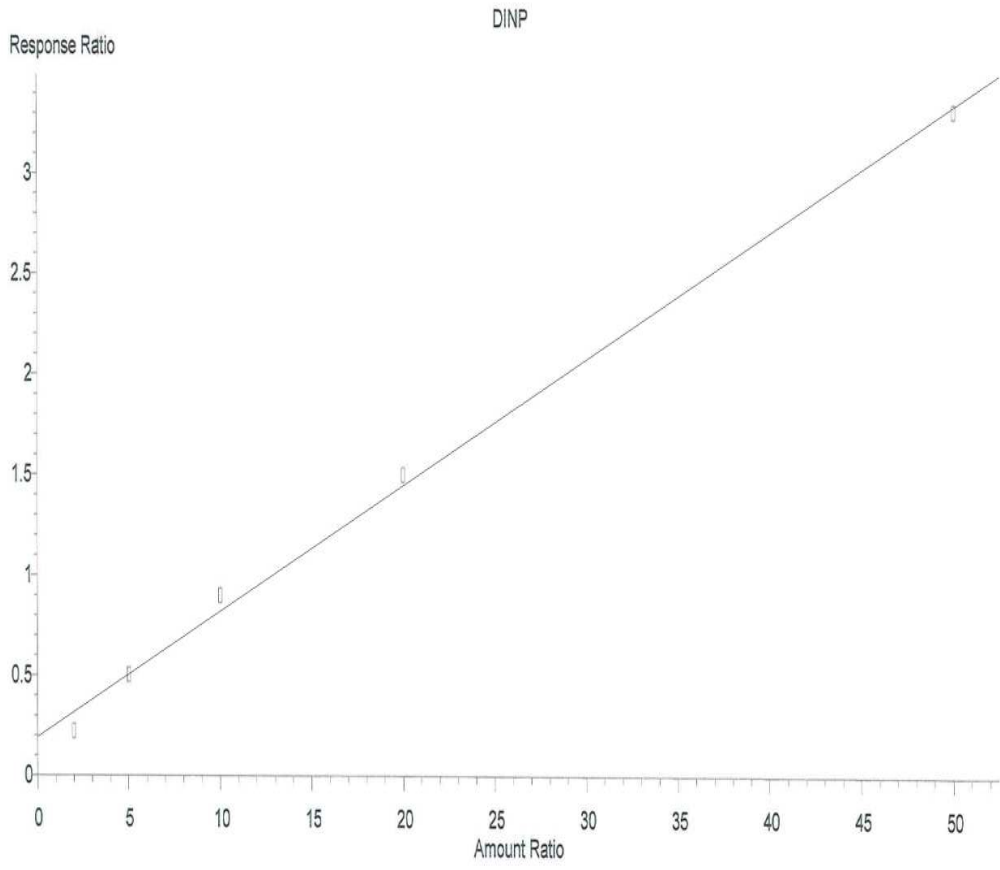


Figure 4.4 : Calibration data of DINP.

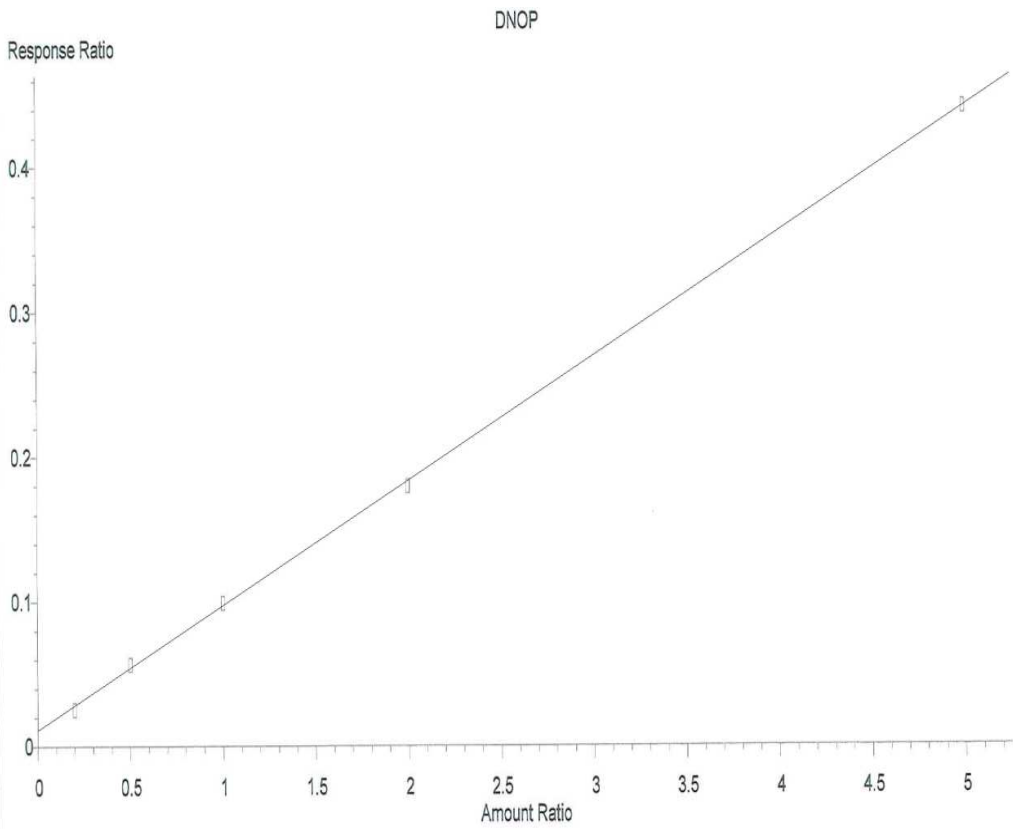


Figure 4.5 : Calibration data of DNOP.

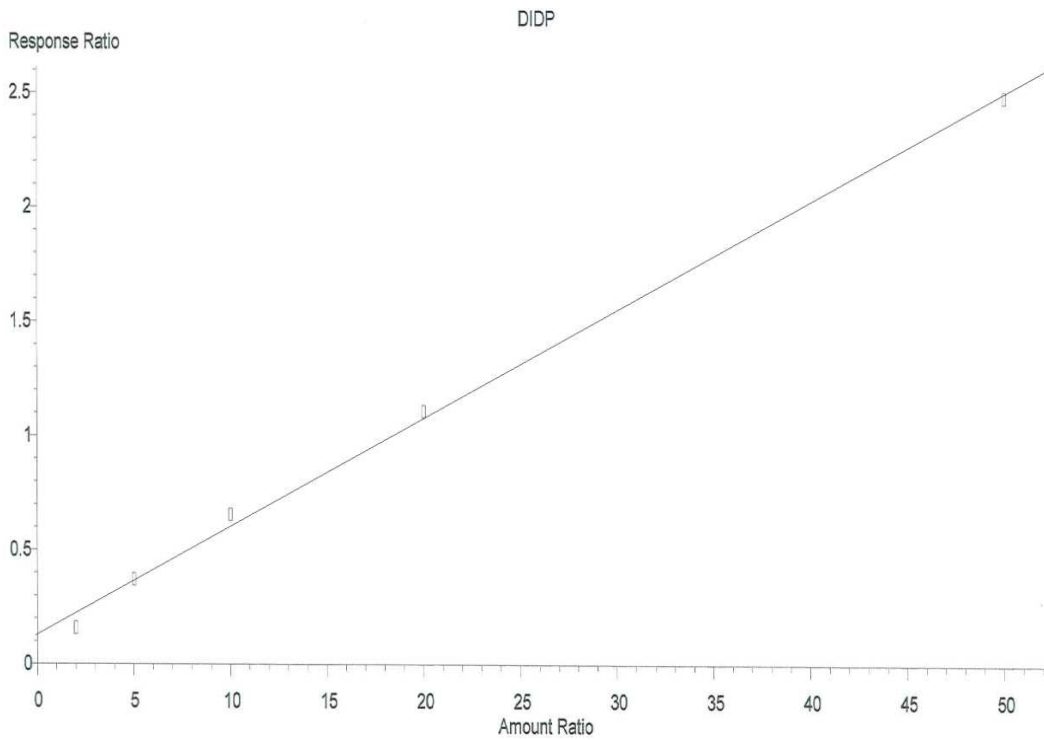


Figure 4. 6 : Calibration data of DIDP.

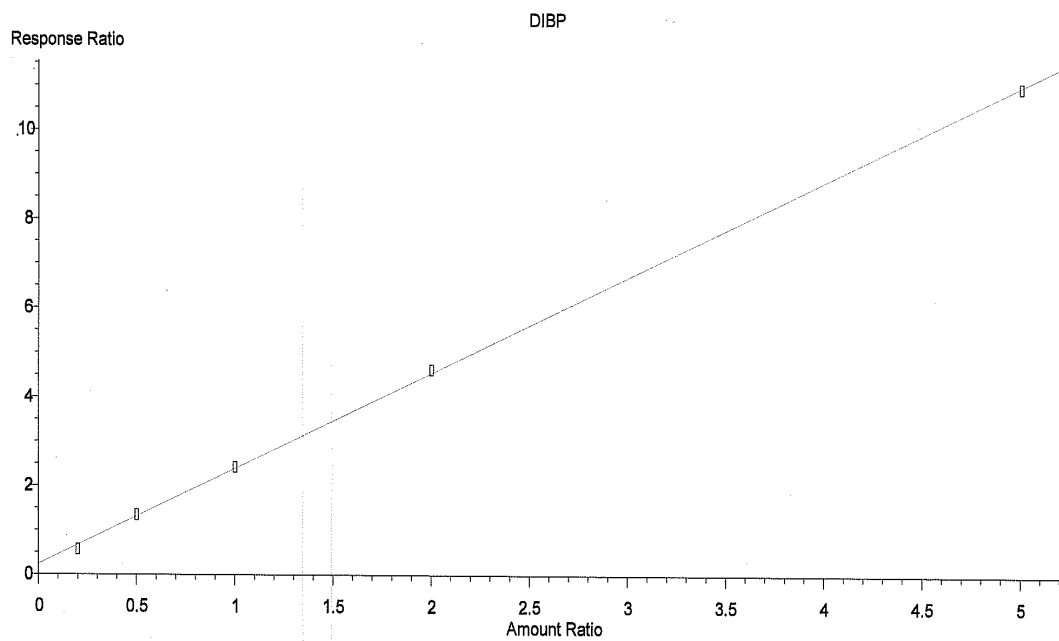


Figure 4. 7: Calibration data of DIBP.

GC-MS retention times with quantifying ions for seven phthalates and internal standard is also given in Table 4.1.

Table 4. 1 : GC–MS retention times with quantifying ions.

| Compound | R.T | O. Ion |
|----------|--------|--------|
| BB | 7.713 | 105 |
| DEHP | 10.181 | 149 |
| DBP | 8.306 | 149 |
| BBP | 9.606 | 149 |
| DINP | 11.188 | 293 |
| DNOP | 10.849 | 279 |
| DIDP | 11.716 | 307 |
| DIBP | 7.981 | 149 |

GS-MS analysis results of six samples prepared by microwave extraction method shown in Table 4.2.

Table 4. 2 : GC-MS analysis results of the microwave extracted samples.

| Sample | Concentration (ppm) | | | | | | |
|--------|---------------------|------|------|------|------|------|------|
| | DEHP | DBP | BBP | DINP | DNOP | DIDP | DIBP |
| 1 | 0.09 | - | - | - | - | - | - |
| 2 | 0.46 | - | - | - | - | - | 0.10 |
| 3 | - | - | - | - | - | - | - |
| 4 | 0.07 | - | - | - | - | - | - |
| 5 | 0.13 | - | - | - | - | - | - |
| 6 | 233000 | 0.23 | 0.45 | - | - | - | 0.03 |

4.1 The Analysis Results

For identifying the content of DIBP, DBP, BBP, DEHP, DNOP, DINP, DIDP phthalates in the samples selected from various polymeric materials from a washing machine that given in Figure 3.1 with GC-MS, calibration curves were plotted using the methods described in Section 3.4.1 and then quantitative analysis were performed. Additionally characterization of structures of these polymeric materials were performed with FTIR spectrum.

4.1.1 Sample No. 1

The FT-IR spectra of sample 1 (black hose) is matched with the resin spectra from the literature library as seen in Figure 4.9. As known it is an EPDM based material and it is confirmed with the FT-IR spectra. Method 1 used GC-MS test result of the sample 1 (shown in Table 4.2) indicates that no phthalates have been found except a very small amount of DEHP.

4.1.2 Sample No. 2

In Figure 4.10 the FT-IR spectra of sample 2 (grey hose, known as PE based material) is matched with the polyethylene spectra from the literature library. There is no significant phthalate peaks for the grey hose as expected. Negligible amounts of DIBP and DEHP are found and shown in Table 4.2.

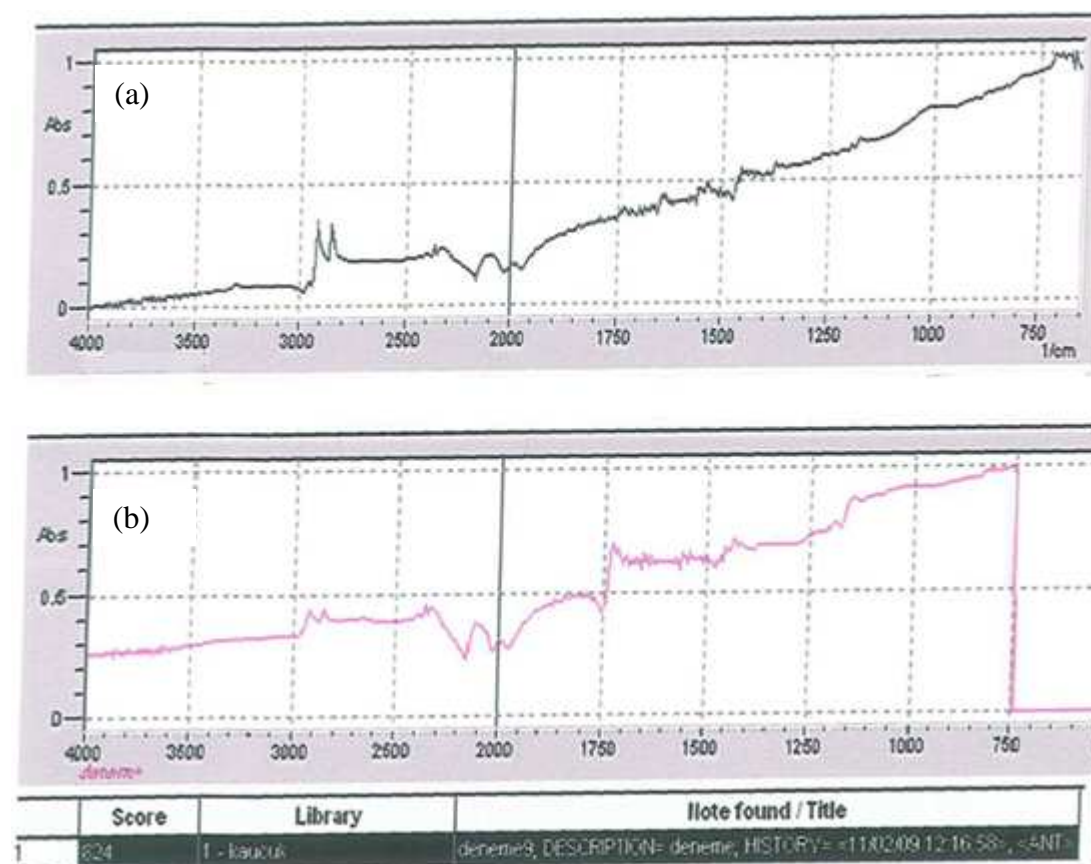


Figure 4. 8 : FT-IR spectra of Sample No.1 (a) Analysis result (b) Literature library result.

4.1.3 Sample No. 3

In Figure 4.11 spectra of bellow, which has an especial formulation containing resin and other some materials, is particularly matched with the polyurethane spectra from

the literature library. As seen in Table 4.2 there is no phthalate peaks found in GC-MS analysis.

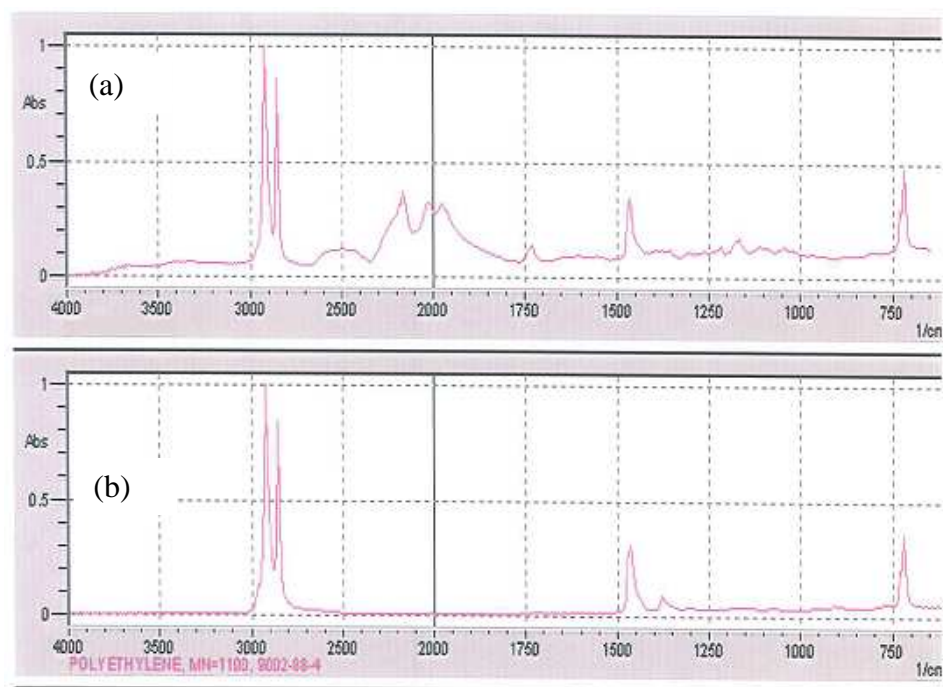


Figure 4. 9 : FT-IR spectra of Sample No.2 (a) Analysis result (b) Literature library result.

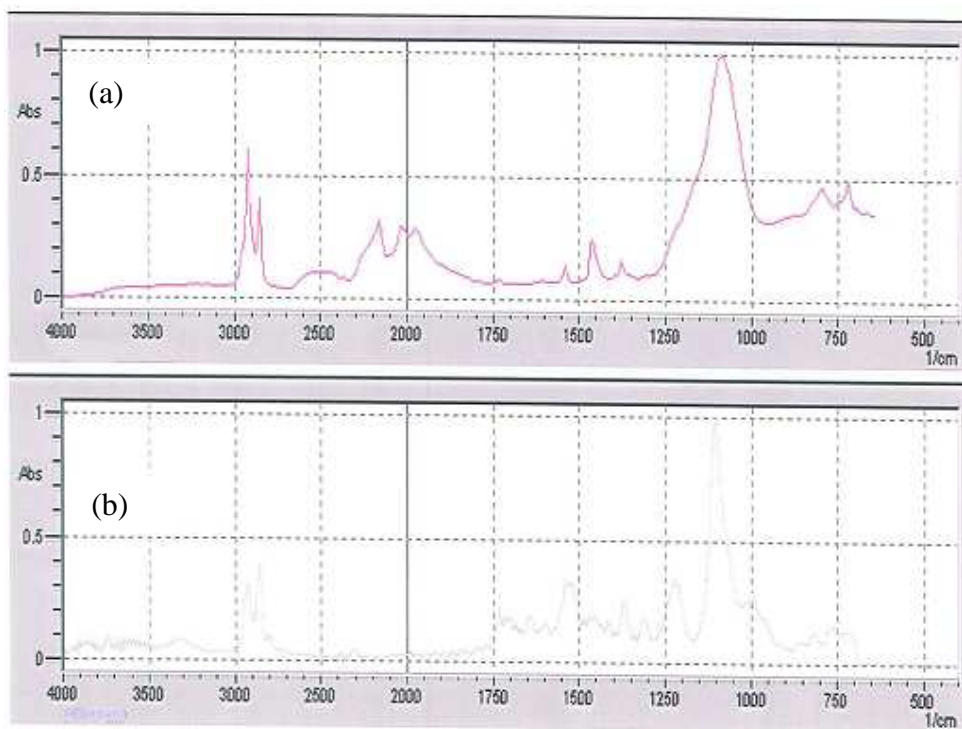


Figure 4. 10 : FT-IR spectra of Sample No.3 (a) Analysis result (b) Literature library result.

4.1.4 Sample No. 4

In Figure 4.12 the FT-IR spectra of sample 4 (vent hose, known as resin based material) is confirmed with the resin spectra from the literature library. There is no significant phthalate peaks as expected. Negligible amounts of DEHP may be found and shown in Table 4.2.

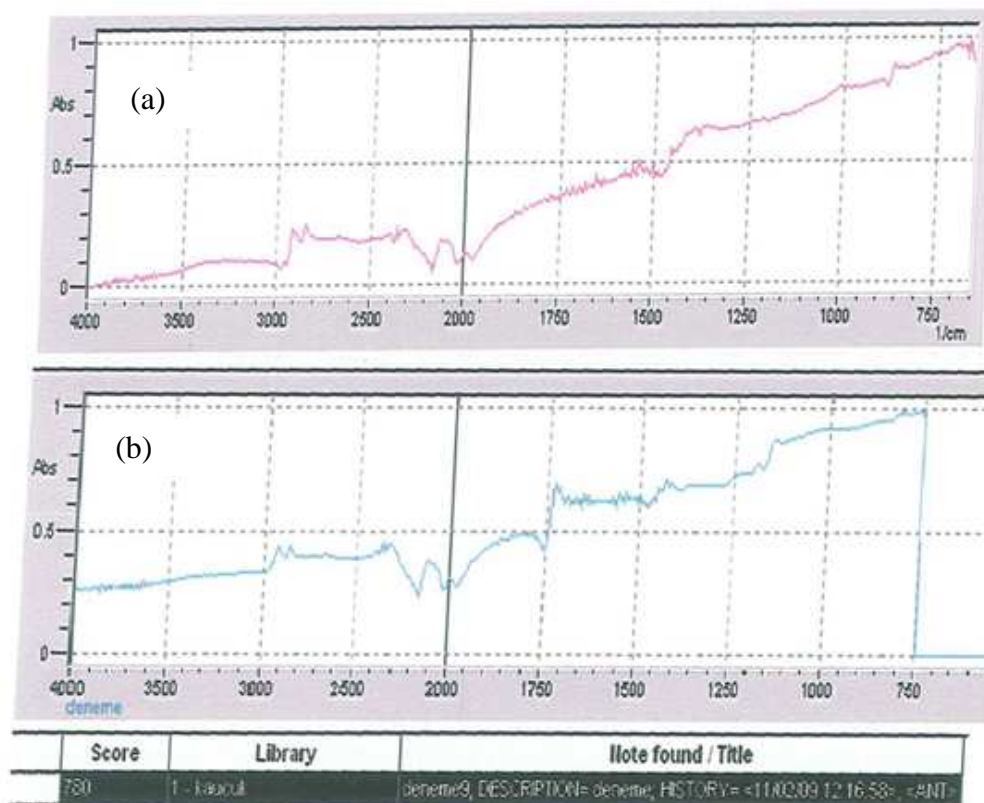


Figure 4. 11: FT-IR spectra of Sample No.4 (a) Analysis result (b) Literature library result.

4.1.5 Sample No. 5

In Figure 4.13 FT-IR spectra of gasket (sample 5) which is matched with PA material is given. In GC-MS results there is no significant phthalate peaks as expected. Negligible amounts of DEHP may be found and shown in Table 4.2.

4.1.6 Sample No. 6

The PVC cable FT-IR spectra is shown in Figure 4.14 and matched with PVC polymer spectra from the library. According to the GC-MS results, the sample (prepared using method 1) contains 4 types of phthalates (DIBP, DBP, BBP and mostly DEHP). DEHP concentration is very high as expected. Because DEHP is the

most common plasticizer for PVC and it can also used with other phthalates like this sample as well as using seperately.

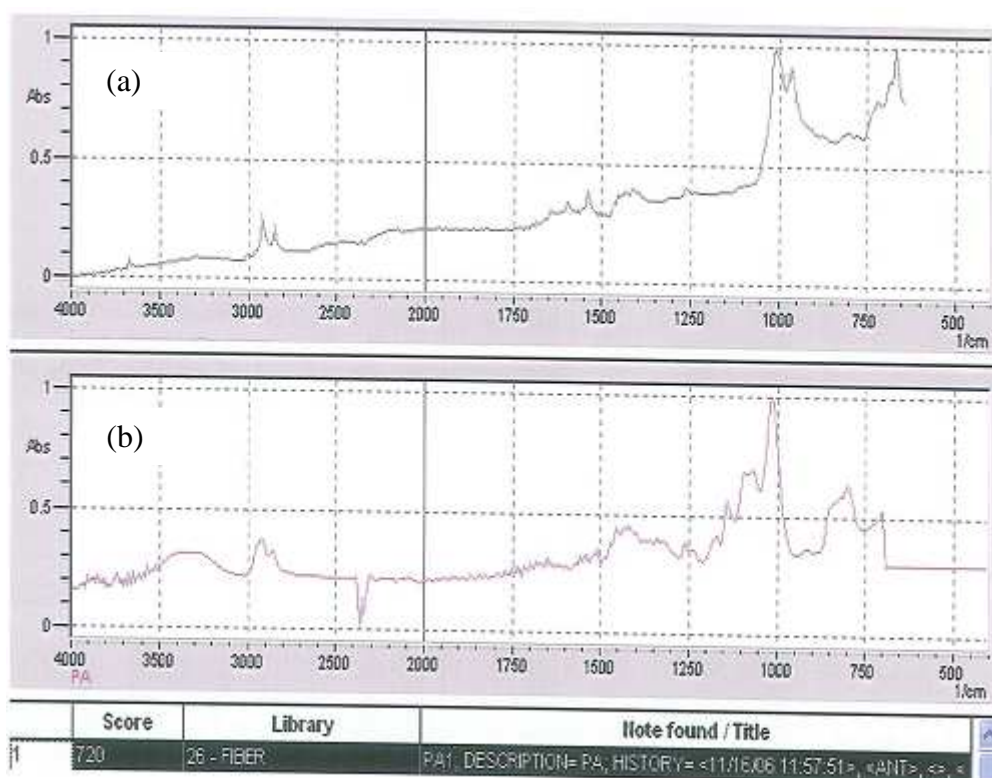


Figure 4. 12: FT-IR spectra of Sample No.5 (a) Analysis result (b) Literature library result.

Finally the GC-MS analysis is repeated for cable sample for using preparation method 2 (soxhlet extraction). According to the results shown in Table 4.3, microwave extraction method is more suitable than soxhlet extraction. Because it can be seen that more concentrations of DEHP can be extracted from the sample in a shorter time.

Table 4. 3 : GC-MS result comparison of cable according to extraction methods.

| Method | Concentration (ppm) | | | | | | |
|------------------|---------------------|------|------|------|------|------|------|
| | DEHP | DBP | BBP | DINP | DNOP | DIDP | DIBP |
| Microwave | 233000 | 0.23 | 0.45 | - | - | - | 0.03 |
| Soxhlet | 228500 | 0.73 | 0.17 | - | - | - | 0.03 |

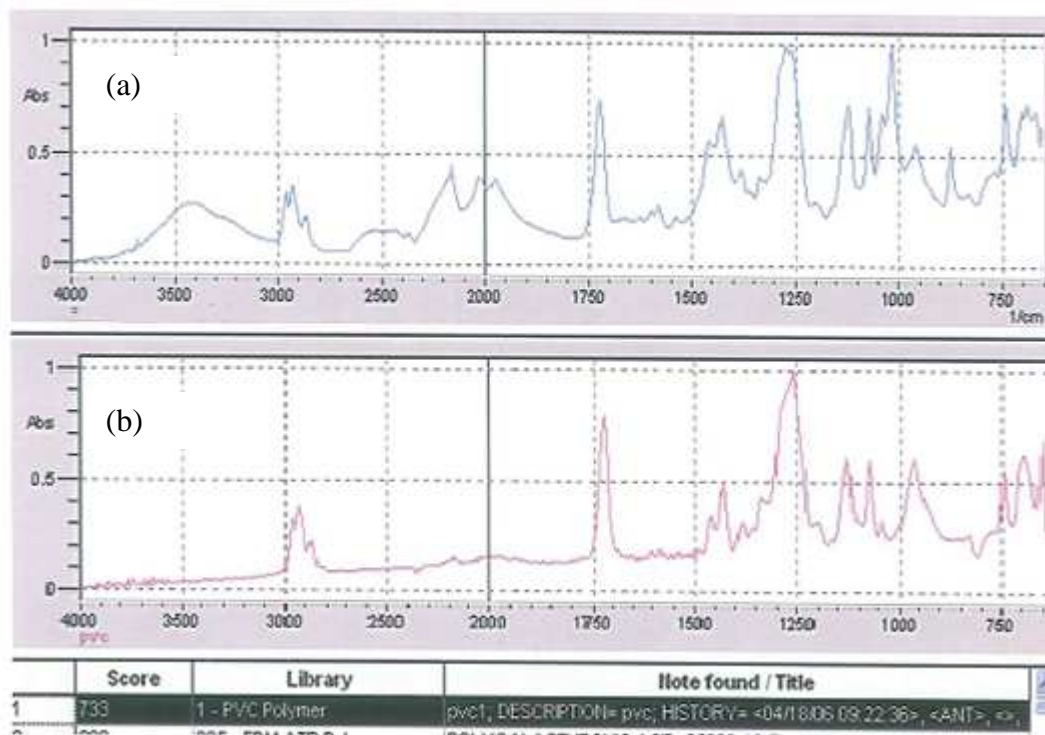


Figure 4. 13: FT-IR spectra of Sample No.6 (a) Analysis result (b) Literature library result.

5. CONCLUSION

The parts of some polymeric materials selected from a washing machine which brand belongs to another than Arçelik were identified by FT-IR analysis and analysed with GC-MS for phthalate contents.

For phthalate identification, seven phthalate esters standards (DIBP, DBP, BBP, DEHP, DNOP, DINP and DIDP) were used to develop a analysis method and calibration curves were plotted. Retention times of these phthalates were also procured.

Six samples were selected from a washing machine parts and analysed by FTIR for material identification and GC-MS for phthalate content.

According to FTIR results, Sample 1 was found as EPDM (or another resin type) based, Sample 2 was found as PE based, Sample 3 and 4 were found as resin based and Sample 5 were found as PVC based materials.

For GC-MS analysis, samples were prepared with microwave extraction and tested, the results of phthalate contents of samples were given in Table 4.2. The samples except Sample 6, comply with REACH because of the SVHC phthalate contents were found under the limits. Sample 6 contains DEHP above the concentration limits in addition to containing four types of phthalates.

The critical Sample 6 were also soxhlet extracted and analysed by GC-MS again. The comparison of microwave and soxhlet extraction methods was given in Table 4.3. In comparison results it was seen that the sample preparation methods is a critical point of the GC-MS analysis. Because analysed DEHP content with microwave extraction was higher than analysed with soxhlet extraction. Soxhlet extraction took much time (nearly six times higher) than microwave extraction. These are the disadvantages of soxhlet method.

As a result, whatever methods were used, the PVC based material Sample 6 was found as non-compliant because of DEHP content above the limits for SVHCs in scope of REACH according to the GC-MS experimental analysis.

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APPENDICES

APPENDIX A: SVHC List

APPENDIX B: Potential usages of SVHCs in white appliances and consumer electronics

APPENDIX A

Table A.1 : SVHC List.

| Name | EC Number | CAS Number | Date of inclusion |
|---|------------------|-------------------|--------------------------|
| Zirconia Aluminosilicate Refractory Ceramic Fibres <i>are fibres covered by index number 650-017-00-8 in Annex VI, part 3, table 3.1 of Regulation (EC) No 1272/2008 of the European Parliament and of the Council of 16 December 2008 on classification, labelling and packaging of substances and mixtures</i> | - | - | 19.12.2011 |
| Calcium arsenate | 231-904-5 | 7778-44-1 | 19.12.2011 |
| Bis(2-methoxyethyl) ether | 203-924-4 | 111-96-6 | 19.12.2011 |
| Aluminosilicate Refractory Ceramic Fibres <i>are fibres covered by index number 650-017-00-8 in Annex VI, part 3, table 3.1 of Regulation (EC) No 1272/2008 of the European Parliament and of the Council of 16 December 2008 on classification, labelling and packaging of substances and mixtures</i> | - | - | 19.12.2011 |
| Potassium hydroxyoctaoxodizincatedichromate | 234-329-8 | 11103-86-9 | 19.12.2011 |
| Lead dipicrate | 229-335-2 | 6477-64-1 | 19.12.2011 |
| N,N-dimethylacetamide | 204-826-4 | 127-19-5 | 19.12.2011 |
| Arsenic acid | 231-901-9 | 7778-39-4 | 19.12.2011 |
| 2-Methoxyaniline; o-Anisidine | 201-963-1 | 90-04-0 | 19.12.2011 |
| Trilead diarsenate | 222-979-5 | 3687-31-8 | 19.12.2011 |
| 1,2-dichloroethane | 203-458-1 | 107-06-2 | 19.12.2011 |
| Pentazinc chromate octahydroxide | 256-418-0 | 49663-84-5 | 19.12.2011 |
| Formaldehyde, oligomeric reaction products with aniline | 500-036-1 | 25214-70-4 | 19.12.2011 |
| Bis(2-methoxyethyl) phthalate | 204-212-6 | 117-82-8 | 19.12.2011 |

Table A.1 (continued) : SVHC List.

| Name | EC Number | CAS Number | Date of inclusion |
|--|-----------------------|------------------------|--------------------------|
| 4-(1,1,3,3-tetramethylbutyl)phenol | 205-426-2 | 140-66-9 | 19.12.2011 |
| Lead diazide, Lead azide | 236-542-1 | 13424-46-9 | 19.12.2011 |
| Phenolphthalein | 201-004-7 | 77-09-8 | 19.12.2011 |
| Dichromium tris(chromate) | 246-356-2 | 24613-89-6 | 19.12.2011 |
| Lead styphnate | 239-290-0 | 15245-44-0 | 19.12.2011 |
| 2,2'-dichloro-4,4'-methylenedianiline | 202-918-9 | 101-14-4 | 19.12.2011 |
| Cobalt dichloride | 231-589-4 | 7646-79-9 | 20.06.2011 |
| 1,2,3-Trichloropropane | 202-486-1 | 96-18-4 | 20.06.2011 |
| 1,2-Benzenedicarboxylic acid, di-C7-11-branched and linear alkyl esters | 271-084-6 | 68515-42-4 | 20.06.2011 |
| 1-Methyl-2-pyrrolidone | 212-828-1 | 872-50-4 | 20.06.2011 |
| Hydrazine | 206-114-9 | 302-01-2 / 7803-57-8 | 20.06.2011 |
| Strontium chromate | 232-142-6 | 7789-06-2 | 20.06.2011 |
| 2-Ethoxyethyl acetate | 203-839-2 | 111-15-9 | 20.06.2011 |
| 1,2-Benzenedicarboxylic acid, di-C6-8-branched alkyl esters, C7-rich | 276-158-1 | 71888-89-6 | 20.06.2011 |
| Chromic acid, Oligomers of chromic acid and dichromic acid, Dichromic acid | 231-801-5 - 236-881-5 | 7738-94-5 - 13530-68-2 | 15.12.2010 |
| Cobalt(II) carbonate | 208-169-4 | 513-79-1 | 15.12.2010 |
| Cobalt(II) diacetate | 200-755-8 | 71-48-7 | 15.12.2010 |
| 2-Methoxyethanol | 203-713-7 | 109-86-4 | 15.12.2010 |
| Chromium trioxide | 215-607-8 | 1333-82-0 | 15.12.2010 |
| Cobalt(II) dinitrate | 233-402-1 | 10141-05-6 | 15.12.2010 |
| Cobalt(II) sulphate | 233-334-2 | 10124-43-3 | 15.12.2010 |

Table A.1 (continued) : SVHC List.

| Name | EC Number | CAS Number | Date of inclusion |
|--|--------------------------|--|--------------------------|
| 2-Ethoxyethanol | 203-804-1 | 110-80-5 | 15.12.2010 |
| Disodium tetraborate, anhydrous | 215-540-4 | 1303-96-4/ 1330-43-4/ 12179-04- 3 | 18.06.2010 |
| Ammonium dichromate | 232-143-1 | 05.09.7789 | 18.06.2010 |
| Tetraboron disodium heptaoxide, hydrate | 235-541-3 | 12267-73- 1 | 18.06.2010 |
| Potassium dichromate | 231-906-6 | 7778-50-9 | 18.06.2010 |
| Trichloroethylene | 201-167-4 | 79-01-6 | 18.06.2010 |
| Sodium chromate | 231-889-5 | 03.11.7775 | 18.06.2010 |
| Potassium chromate | 232-140-5 | 7789-00-6 | 18.06.2010 |
| Boric acid | 233-139-2 / 234-343-4 | 10043-35- 3 / 11113- 50-1 | 18.06.2010 |
| Acrylamide | 201-173-7 | 79-06-1 | 30.03.2010 |
| Lead chromate molybdate sulphate red (C.I. Pigment Red 104) | 235-759-9 | 12656-85- 8 | 13.01.2010 |
| Lead chromate | 231-846-0 | 7758-97-6 | 13.01.2010 |
| Anthracene oil, anthracene-low | 292-604-8 | 90640-82- 7 | 13.01.2010 |
| 2,4-Dinitrotoluene | 204-450-0 | 121-14-2 | 13.01.2010 |
| Anthracene oil, anthracene paste, anthracene fraction | 295-275-9 | 91995-15- 2 | 13.01.2010 |
| Anthracene oil | 292-602-7 | 90640-80- 5 | 13.01.2010 |
| Tris(2-chloroethyl)phosphate | 204-118-5 | 115-96-8 | 13.01.2010 |
| Aluminosilicate Refractory Ceramic Fibres <i>are fibres covered by index number 650-017-00-8 in Annex VI, part 3, table 3.2 of Regulation (EC) No 1272/2008 of the European Parliament and of the Council of 16 December 2008 on classification, labelling and packaging of substances and mixtures</i> | - | Extracted from Index no.: 650- 017-00-8 | 13.01.2010 |

Table A.1 (continued) : SVHC List.

| Name | EC Number | CAS Number | Date of inclusion |
|--|----------------------------|--|--------------------------|
| Anthracene oil, anthracene paste, distn. lights | 295-278-5 | 91995-17-4 | 13.01.2010 |
| Zirconia Aluminosilicate Refractory Ceramic Fibres <i>are fibres covered by index number 650-017-00-8 in Annex VI, part 3, table 3.1 of Regulation (EC) No 1272/2008 of the European Parliament and of the Council of 16 December 2008 on classification, labelling and packaging of substances and mixtures</i> | - | Extracted from Index no. 650-017-00-8 | 13.01.2010 |
| Pitch, coal tar, high temp. | 266-028-2 | 65996-93-2 | 13.01.2010 |
| Lead sulfochromate yellow (C.I. Pigment Yellow 34) | 215-693-7 | 1344-37-2 | 13.01.2010 |
| Diisobutyl phthalate | 201-553-2 | 84-69-5 | 13.01.2010 |
| Anthracene oil, anthracene paste | 292-603-2 | 90640-81-6 | 13.01.2010 |
| Sodium dichromate | 234-190-3 | 7789-12-0/ 10588-01-9 | 28.10.2008 |
| 5-tert-butyl-2,4,6-trinitro-m-xylene (musk xylene) | 201-329-4 | 81-15-2 | 28.10.2008 |
| 4,4'-Diaminodiphenylmethane (MDA) | 202-974-4 | 101-77-9 | 28.10.2008 |
| Bis(tributyltin)oxide (TBTO) | 200-268-0 | 56-35-9 | 28.10.2008 |
| Triethyl arsenate | 427-700-2 | 15606-95-8 | 28.10.2008 |
| Dibutyl phthalate (DBP) | 201-557-4 | 84-74-2 | 28.10.2008 |
| Diarsenic trioxide | 215-481-4 | 1327-53-3 | 28.10.2008 |
| Anthracene | 204-371-1 | 120-12-7 | 28.10.2008 |
| Alkanes, C10-13, chloro (Short Chain Chlorinated Paraffins) | 287-476-5 | 85535-84-8 | 28.10.2008 |
| Lead hydrogen arsenate | 232-064-2 | 7784-40-9 | 28.10.2008 |
| Benzyl butyl phthalate (BBP) | 201-622-7 | 85-68-7 | 28.10.2008 |
| Hexabromocyclododecane (HBCDD) and all major diastereoisomers identified: | 247-148-4 and 221-695-9 | 25637-99-4 3194-55-6 (134237-50-6) (134237-51-7) (134237-52-8) | 28.10.2008 |

Table A.1 (continued) : SVHC List.

| Name | EC Number | CAS Number | Date of inclusion |
|---------------------------------------|----------------------|-----------------------|--------------------------|
| Diarsenic pentaoxide | 215-116-9 | 1303-28-2 | 28.10.2008 |
| Bis (2-ethylhexyl)phthalate (DEHP) | 204-211-0 | 117-81-7 | 28.10.2008 |

APPENDIX B

Table B. 1 : Potential usages of SVHCs in white appliances and consumer electronics.

| Substance | Potential Usages | Investigation |
|---|---------------------------|--|
| Zirconia Aluminosilicate Refractory Ceramic Fibres | Refractory ceramic fibres | glass ceramic hobs, electric ovens, electric grills, microwave ovens, in gas-fired apparatus or other devices with “open” flames |
| Aluminosilicate Refractory Ceramic Fibres | Refractory ceramic fibres | glass ceramic hobs, electric ovens, electric grills, microwave ovens, in gas-fired apparatus or other devices with “open” flames |
| Calcium arsenate | None | None |
| Bis(2-methoxyethyl) ether | Coatings | articles containing adhesives, paints, coatings |
| Potassium hydroxyoctaoxodizincatedichromate | Paints | Paint coated components |
| Lead dipicrate | None | None |
| N,N-dimethylacetamide (DMAC) | Man-made fibres | Man-made fibre contained components |
| Arsenic acid | None | None |
| 2-Methoxyaniline; o-Anisidine | printing ink | printing inks for packing materials like paper, cardboard, polymer and aluminum foil |
| Trilead diarsenate | None | None |
| 1,2-dichloroethane | None | None |
| Pentazinc chromate octahydroxide | Coating powders | Coating powders |
| Formaldehyde, oligomeric reaction products with aniline (technical MDA) | Epoxy resins | Epoxy resins and adhesives |

Table B. 1 (continued) : Potential usages of SVHCs in white appliances and consumer electronics.

| Substance | Potential Usages | Investigation |
|--|--|---|
| Bis(2-methoxyethyl) phthalate | Plasticizer | Enamelled wire, film, high-strength varnish and adhesive. |
| 4-(1,1,3,3-tetramethylbutyl)phenol | phenolic resins, paints, rubber | Adhesives, rubber components, paints |
| Lead diazide | None | None |
| Phenolphthalein | None | None |
| Dichromium tris(chromate) | metal treatment | Anticorrosive metal coatings |
| Lead styphnate | None | None |
| 2,2'-dichloro-4,4'-methylenedianiline (MOCA) | PU | polyurethane resins, polyurethane elastomers, epoxy resins and epoxy urethane resins |
| 2,4-Dinitrotoluene | PU foam production | Diisocyanate impurities used in PU foam production |
| 4,4'-Diaminodiphenylmethane (MDA) | PU foam production Hardener in rubber and epoxy | MDA impurities used in PU foam production Hardeners for epoxy and rubber |
| 5-tert-butyl-2,4,6-trinitro-m-xylene (musk xylene) | None | None |
| Acrylamide | Polyacrylamide | Polyacrylamide materials |
| Alkanes, C10-13, chloro (Short Chain Chlorinated Paraffins) | Flame retardant in rubber | Leak proof parts of washing machine, dishwasher, refridgerators and other rubber parts: hoses, bellows etc. |
| Aluminosilicate Refractory Ceramic Fibres (SiO ₂ , Al ₂ O ₃) | None | None |
| Ammonium dichromate | TV display | Raster scan |

Table B. 1 (continued) : Potential usages of SVHCs in white appliances and consumer electronics.

| Substance | Potential Usages | Investigation |
|--|--|--|
| Anthracene Anthracene oil Anthracene oil, anthracene paste Anthracene oil, anthracene paste, anthracene fraction Anthracene oil, anthracene paste, distn. Lights Anthracene oil, anthracene-low | Pigments Electronic components Liquid crystallines | Colorants in cables Powder paints LCD displays Semiconductor electronic components (transistor, diode etc.) |
| Benzyl butyl phthalate Bis (2-ethyl (hexyl) phthalate) Dibutyl phthalate Diisobutyl phthalate | PVC plasticizer | PVC parts (cables, hoses etc.) |
| Bis(tributyltin)oxide | Biocides | Wooden parts |
| Boric Acid | Fiberglass TV | Fiberglass reinforced materials LCD flat panels |
| Disodium tetraborate, anhydrous Tetraboron disodium heptaoxide, hydrate | Fiberglass Adhesive | Fiberglass reinforced materials Adhesives (PVA etc.) |
| Diarsenic pentaoxide Diarsenic trioxide | Glass Cable Biocides | Glass parts Wooden parts Cable covers |
| Hexabromocyclododecane (HBCDD) | PS flame retardant | EPS, XPS, HIPS parts |
| Cobalt dichloride | Paint | Paints |
| Lead chromate Lead chromate molybdate sulphate red Lead sulfochromate yellow | Paint | Colourful plastic parts, masterbatch colorants |
| Lead hydrogen arsenate | None | None |
| Potassium dichromate Potassium chromate Sodium dichromate Sodium chromate | Anticorrosive Metal coating | Anticorrosive metal parts |
| Trichloroethylene | None | None |

Table B. 1 (continued) : Potential usages of SVHCs in white appliances and consumer electronics.

| Substance | Potential Usages | Investigation |
|--|---|---|
| Triethyl arsenate | Semiconductors | Semiconductor electronic parts (transistor, diode) |
| tris(2-chloroethyl) phosphate | Flame retardant | PU,PVC, elastomer, epoxy parts and adhesives |
| Pitch, coal tar, high temp. | Active carbon production | Odour adsorbents |
| Zirconia Aluminosilicate, Refractory Ceramic Fibres | None | None |
| Cobalt(II) sulphate | Anticorrosive | Anticorrosive metal parts |
| Cobalt(II) dinitrate | Batteries | Rechargeable batteries, Ni-Cd pil, Ni-MH batteries |
| Cobalt(II) carbonate | Enamel | Enamel parts |
| Cobalt(II) diacetate | None | None |
| 2-Methoxyethanol | None | None |
| 2-Ethoxyethanol | None | None |
| Chromium trioxide | Electronic components HDPE,LLDPE,PP | Electronic components HDPE,LLDPE,PP parts |
| Chromic acid, Oligomers of chromic acid and dichromic acid, Dichromic acid | None | None |
| 2-Etoksietil Asetat (2-EEA) | None | None |
| Strontium chromate | Yellow paint PVC Al and steel coating | Yellow parts, yellow PVC parts Anticorrosive Al and steels |

Table B. 1 (continued) : Potential usages of SVHCs in white appliances and consumer electronics.

| Substance | Potential Usages | Investigation |
|---|-------------------------|------------------------------|
| 1,2-Benzenedicarboxylic acid, di-C7-11-branched and linear alkyl esters (DHNUP) | PVC plasticizer | PVC components (cables etc.) |
| 1,2-Benzenedicarboxylic acid, di-C6-8-branched alkyl esters, C7-rich (DIHP) | | |
| Hydrazine | None | None |
| 1-Methyl-2-pyrrolidone (NMP) | None | None |
| 1,2,3-Trichloropropane (1,2,3-TCP) | None | None |

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