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MARMARA UNIVERSITY
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CFC-11 AMOUNT IN POLYURETHANE FOAM IN END-OF-LIFE REFRIGERATORS

Burcu Yazıcı

THESIS
FOR THE DEGREE OF MASTER OF SCIENCE
IN
ENVIRONMENTAL ENGINEERING

SUPERVISOR
Prof. Barış ÇALLI

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Assoc. Prof. Zehra S. Can

ISTANBUL 2012

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January, 2012 **Burcu Yazıcı**

TABLE OF CONTENT

ABSTRACT

CFC-11 AMOUNT IN POLYURETHANE FOAM IN END-OF-LIFE REFRIGERATORS

Refrigerators are among the most widely used household appliances. Insulation is of key importance which is accomplished by polyurethane (PU) foams consisting of a mixture of polyols, isocyanates and blowing agents. Blowing agent limits heat transfer and reduces energy consumption. CFC-11 (trichlorofluoromethane) had been used as blowing agent until its ozone depleting potential was discovered. Its use was then restricted with the Montreal Protocol. Today, CFC-11 and CFC-11 containing substances are regulated under “Directive on Ozone Depleting Substances” and “Regulation for General Principles of Waste Management” in Turkey. In addition, “Waste Electrical and Electronic Equipment Control Regulation” has been prepared and shall enter into force soon. However, the total amount of CFC-11 in PU insulation foam of refrigerators is not certainly known in Turkey. Therefore, this study was conducted to ascertain the amount of CFC-11 in pre-1996 refrigerators in-use and the related ozone depleting potential. Total number of refrigerators containing CFC-11 was determined from domestic sales data for years between 1986 and 1995, and using a survival function, it was obtained that 2.24 million of these refrigerators are still in use. Assuming 4 kg of insulation foam per refrigerator, the total amount of PU foam blown with CFC-11 was calculated as 8944 tons. In order to estimate the amount of CFC-11 in PU foam of pre-1996 refrigerators in-use, foam samples were taken from an obsolete refrigerator and their CFC-11 content was measured. CFC-11 was released by heating the foam samples to 140^{o}C for 48 hours in a closed bottle and analyzed in the headspace using a GC-MS. As a result, by assuming that 2.24-million pre-1996 refrigerators are still in-use, the total amount of CFC-11 in insulation foam of refrigerators in Turkey was estimated to be 1011-1078 tons.

January, 2012 **Burcu YAZICI**

ÖZET

ÖMRÜNÜ TAMAMLAMIŞ BUZDOLAPLARINDA BULUNAN POLİÜRETAN KÖPÜKTEKİ CFC-11 MİKTARI

Buzdolapları yaygın olarak kullanılan beyaz eşyalar arasındadır. Önemli unsurların başında gelen yalıtım; poliol, izosiyanat ve kabartıcının karışımından oluşan poliüretan köpük ile gerçekleştirilir. Kabartıcı, ısı transferini engeller ve enerji tüketimini azaltır. CFC-11, ozon tüketme potansiyeli belirlene kadar kabartıcı olarak kullanılmıştır. Sonrasında ise kullanımı Montreal Protokolü ile kısıtlanmıştır. Günümüzde, CFC-11 ve CFC-11 içeren maddeler "Ozon Tabakasını İncelten Maddeler" ve "Atık Yönetimi Genel Esaslarına İlişkin Yönetmelik" ile düzenlenmektedir. Buna ek olarak, "Atık Elektrikli ve Elektronik Ekipmanların Kontrolü Yönetmeliği" de taslak halinde olup, yakında yürürlüğe girecektir. Fakat buzdolaplarındaki PU köpük içindeki CFC-11 miktarı bilinmemektedir. Bu nedenle, bu çalışma 1996 öncesi üretilmiş ve halen kullanımda olan buzdolaplarındaki CFC-11 miktarını ve buna ilişkin ozon tüketme potansiyelini tespit etmek için gerçekleştirilmiştir. CFC-11 içeren buzdolabı miktarını tespit etmek için 1986-1995 arası üretilmiş buzdolabı iç satış verileri incelenmiş, basit bir model yardımıyla, 2,24 milyon buzdolabının halen kullanımda olduğu belirlenmiştir. Bir buzdolabında 4 kg yalıtım köpüğü bulunduğu göz önüne alınarak, CFC-11 içeren toplam PU köpük miktarı 8944 ton olarak hesaplanmıştır. 1996 öncesi üretilmiş, halen kullanımda olan buzdolaplarındaki PU köpük içindeki CFC-11 miktarını belirlemek için, ömrünü tamamlamış bir buzdolabından köpük numuneleri alınmış ve bu numunelerin CFC-11 içeriği ölçülmüştür. Köpük numuneleri ağzı kapalı bir şişede, 140^{o}C sıcaklıkta 48 saat bekletilerek CFC-11 açığa çıkartılmış ve GC-MS ile analiz edilmiştir. Sonuç olarak, Türkiye'de, 1996 öncesi üretilmiş ve halen kullanımda olan buzdolabı miktarı 2,24 milyon olarak kabul edildiğinde, buzdolaplarında, yalıtım köpüğünde bulunan toplam CFC-11 miktarının 1011-1078 ton olması beklenmektedir.

Ocak, 2012 **Burcu YAZICI**

ABBREVIATIONS

BA **:** Blowing Agent

CFC **:** Chlorofluorocarbon

CFC-11 **:** Trichlorofluoromethane

CFC-12 **:** Dichlorodifluoromethane

GCMS **:** Gas Chromatography-Mass Spectroscopy

HC **:** Hydrocarbon

HCFC **:** Hydrochlorofluorocarbon

HFC **:** Hydrofluorocarbon

ODP **:** Ozone Depletion Potential

ODS **:** Ozone Depleting Substance

PTFE **:** Polytetrafluoroethylene

PU **:** Polyurethane

PUR **:** Rigid Polyurethane Foam

TURKBESD **:** Turkish Association of Household Appliances Manufacturers

VIP **:** Vacuum Insulation Panel

WEEE **:** Waste Electrical and Electronic Equipment

LIST OF FIGURES

LIST OF TABLES

CHAPTER I

INTRODUCTION

Waste electrical and electronic equipment is becoming a growing problem in Turkey each passing day. Refrigerators are among these electrical equipments consisting of up to 90% recyclable materials such as metals and plastics. However, it is most likely that hazardous substances will be released as well during recycling of these valuable materials, since refrigerators also include polyurethane foams blown with trichlorofluoromethane (CFC-11), a gas with high ozone depleting potential. CFC-11 was used as blowing agent in rigid polyurethane foams for long years due to its excellent insulation properties as well as ease of use. However, it was soon discovered that CFC-11 was among the ozone depleting substances. Consequently, its use was restricted and then banned. The first step was taken with the Montreal Protocol; developed countries ceased the use of CFC-11 by 1996, whereas developing countries continued to use it until 2010. In Turkey, use of CFC-11 in refrigerators was terminated by 1995. However, CFC-11 containing rigid polyurethane foams are an environmental problem still today, considering that the lifetime of a refrigerator varies from 15 to 40 years.

In order to avoid the environmental damage caused by these wastes, “Waste Electrical and Electronic Equipment Control Regulation” has been prepared. According to the regulation, CFCs and polyurethane foams have to be properly recovered and disposed. In addition, waste CFC-11 and rigid polyurethane foams containing CFC-11 are also regulated under “Regulation for General Principles of Waste Management” and considered hazardous waste. Nevertheless, information on the amounts of refrigerators that are to be disposed of in the near future is limited.

The objectives of this study are to determine number of pre-1996 refrigerators in-use containing polyurethane foam blown with CFC-11 and to ascertain the amount of CFC-11 in these refrigerators and its related ozone depleting potential.

CHAPTER II

GENERAL BACKGROUND

II.1 HOUSEHOLD APPLIANCES

II.1.1 History

Household appliances are large machines that accomplish major housekeeping tasks, such as cooking, laundry, dish washing, and preserving foods. Refrigerators, washing machines, dishwashers, freezers, oven, clothes dryers and water heaters are the main major household appliances [1].

The first motor-driven dishwasher was introduced in 1893 at Chicago World Fair. The compartments were placed inside a wheel that lay flat within a copper boiler. A motor turned the wheel while hot soapy water sprayed from the bottom of the boiler and rained down on the dishes. However, dishwashers had not become a standard household appliance until the 1950s [2].

First electric powered washing machine was invented in 1906, whereas the first electrical clothes dryers appeared in 1915 [3]. In 1922, Maytag Corporation introduced the agitator system for moving the water around in the drum. This system is still the most widely used washing technique. The first automatic washing machines were developed in the 1950s [3, 4].

Additionally, first electric oven was produced in 1908, while the first automatic iron was introduced to the market in 1921. Innovations in this field continued with the invention of garbage disposer in 1927 and microwave oven in 1955.

II.1.2 Household Appliances Manufacturing in Turkey

The sector started production as an assembly industry in the 1950s. First facility was established in 1955, whereas the first washing machine and refrigerator were produced in 1959 and 1960, respectively. The industry has achieved tremendous growth since then.

Turkish household appliance manufacturers, which started out as companies working under licensing agreements and then passing over to know-how usage, has today carved out its own niche in world markets with its own design and technology. Major brands in the market are: Arçelik, Beko, Profilo, Bosch, Siemens, Vestel, Ariston and Indesit. Manufacturing facilities are located mostly in the Marmara, Aegean and Central Anatolia regions of Turkey. The main factories are established in İstanbul, Manisa, Eskişehir, Bolu, Ankara and Tekirdağ [5]. Major producers in Turkey and the locations of the manufacturing facilities were given in Figure II. 1.

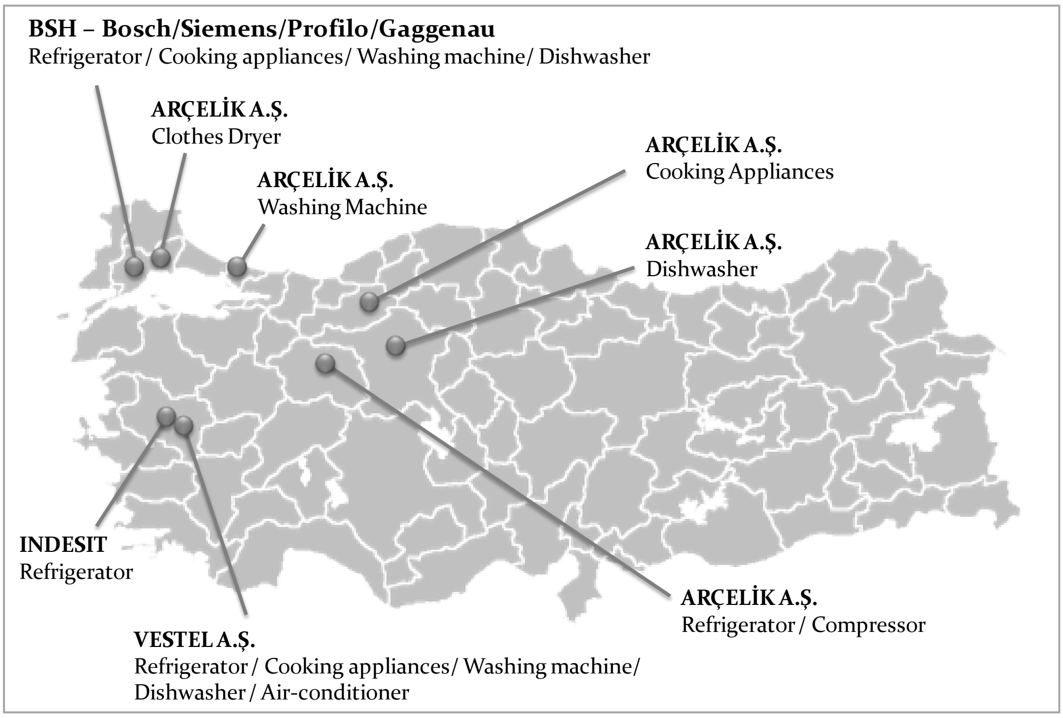

Figure II. 1 Major household appliance manufacturers in Turkey

The household appliances sector in Turkey earned a revenue of USD 8 billion in 2008. Approximately 16 million units were produced of which approximately 12 million were exported, both in 2008 and 2009. Home appliances are mainly exported to European countries such as the UK, France, Germany and Italy. The home appliances industry was hit by the global financial crisis in 2009. Exports decreased by 25 percent and domestic revenue decreased by 30 percent within the last quarter of 2009 when the affects of the crisis were significant [6]. Production numbers of household appliance manufacturers, which are members of TURKBESD, are demonstrated in Table II. 1.

Table II. 1 Production numbers for household appliances industry in Turkey (x1000) [7]

	2005	**2006**	**2007**	**2008**	**2009**	**2010**
Refrigerators	5 498	6 740	6 864	6 002	6 177	7 032
Washing Machines	4 421	5 277	5 128	4 739	5 180	5 767
Dishwashers	783	1 180	1 842	2 140	2 343	2 537
Cooking Appliances	1 660	2 201	2 363	3 039	2 736	3 060
TOTAL	12 362	15 398	16 197	15 920	16 436	18 396

II.1.3 Manufacturing of Household Appliances

The basic processes involving manufacturing of household appliances can be summarized in six steps, which are press/welding, surface finishing/painting, insulation (refrigerators only), plastic molding and assembly. The simplified flow diagram of household appliance manufacturing is given in Figure II. 2.

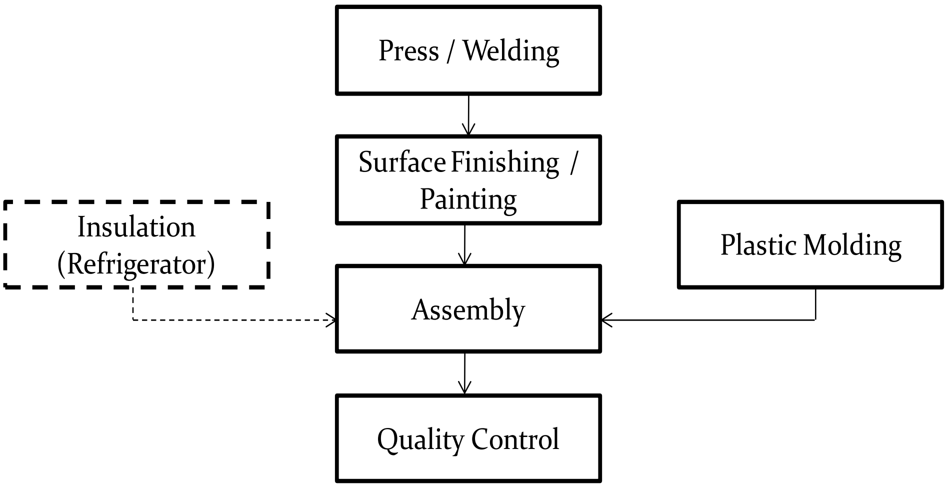

Figure II. 2 Manufacturing Steps for Household Appliances

The first step in manufacturing of household appliances involves forming of sheet metal parts by press. Metal sheets are cut to desired sizes in press machine and are then welded. Prior to painting, welded parts are subject to cleaning procedure where oil, grease and all other contaminants are removed from the surface of the metal [8]. Alkaline cleaning provides an economical and effective alternative to the use of organic solvents to remove greases, oils and waxes [9]. Cleaned metal parts are then treated for corrosion prevention. Zinc phosphating is usually applied for surface treatment and finishing purposes [10]. Phosphating process is applied to the surface of a metal surface in order to form an insoluble, corrosion resistant phosphate layer on the substrate surface. All the phosphating compositions are basically dilute phosphoric acid based solutions containing alkali metal/heavy metal ions in them besides suitable accelerators, since phosphating reaction tends to be slow owing to the polarization caused by the hydrogen evolved in the cathodic reaction. Topochemical reaction takes place once the steel panel is introduced into the phosphating solution. Iron, that is present on the substrate, dissolves at the microanodes in the presence of free phosphoric acid. Meanwhile, hydrogen evolution occurs at the microcathodic sites. The pH at the metal/solution interface increases as a result of formation of soluble primary ferrous phosphate leading to a simultaneous depletion of free acid concentration in the solution. The change in pH affects the hydrolytic equilibrium between the soluble primary phosphates and the insoluble tertiary phosphates of the heavy metal ions in the phosphating solution. Thus, rapid conversion and deposition of insoluble heavy metal tertiary phosphates take place [9]. Once phosphating and painting is finished, metal parts are ready for assembly.

Insulation step is unique to refrigerators, which is applied to avoid heat transfer to the cooled parts. Insulation is provided by polyurethane foam which is a mixture of polyol, isocyanates and blowing agent. Plastic parts of appliances are prepared for assembly in plastic molding. Plastic parts are formed in an injection molding machine which is a metal mold with a shape of the desired part. Plastic is forced into the mold under high pressure after being heated to its melting point. Then, it is subjected to water to cool and solidify the part. The mold is then opened and the part is pulled out [11]. The prepared metal and plastic parts are fitted together in the assembly line. As the final step, assembled appliances are checked for quality and packed for transportation.

II.2 REFRIGERATORS

II.2.1 History of Refrigeration

Refrigerators are one of the most widely used household appliances that are developed to preserve food by storing them at low temperatures. In 1803, the domestic ice box (Figure II. 3) made of wood with suitable insulation was invented and was used for almost 150 years without much modification. Ice was kept at the top of the box so that low temperatures are produced in the box due to heat transfer from ice by natural convection. A drip pan was employed to collect the water due to the melting of ice. The box was refilled with fresh ice once all ice had melted [12].

Figure II. 3 Domestic ice box [13]

Domestic refrigerators using mechanical systems were developed after 1887. General Electric Company introduced the first domestic refrigerator (Figure II. 4) in 1911, followed by Frigidaire in 1915 [12].

Figure II. 4 Electric compression domestic refrigerator [14]

The first refrigerator with any type of automatic control was introduced in 1918 by Kelvinator. Consumers were introduced to freezers when the first electric refrigerators with ice cube compartments came on the market in the 1920s and 1930s. Mass production of modern refrigerators got started only after World War II. Refrigeration technology started to rise in the 1950s and 1960s when innovations like automatic defrost and automatic ice makers first appeared [15].

In the 1970s and 1980s, the environment became a top priority, which led to more energy-efficient refrigerators and elimination of chlorofluorocarbons in refrigeration sealed systems [15].

Household refrigerators consist of two critical components: a refrigerant and thermal insulation. A refrigerant absorbs heat from the refrigerator cabinet space and transfers it outside. Thermal insulation requires highly energy efficient foam blowing agents to limit heat transfer to refrigerated cold spaces and reduce energy consumption [16]. More details can be found in sections II.2.2 and II.2.3.

II.2.2 Refrigerants

The first refrigeration system was introduced in 1881 which was basically a fan blowing wind onto the ice. Mechanical refrigeration systems were developed as a result of shortage for ice due to mild winter conditions in 1889 and 1890 [3].

One of the pioneers of refrigeration was Dr. William Cullen. He conducted studies on liquids that vaporize under vacuum in the 1700s. At the beginning of 1800s, Michael Faraday liquefied ammonia for refrigeration purposes. The system used today is based upon the studies conducted by Faraday. Refrigerant gases are chosen according to their boiling points. Gases that vaporize at low boiling points are preferred, since their heat absorption capacity is much higher [3]. The working principle of a refrigerator is as follows (Figure II. 5):

1. The refrigerant enters the expansion valve as liquid. As it passes through the valve, the sudden drop in pressure makes it expand, cool, and turn into a gas.
2. As the coolant flows around the chiller cabinet, it absorbs and removes heat from the food inside.
3. The compressor squeezes the coolant, raising its temperature and pressure.
4. The refrigerant flows through thin pipes on the back of the fridge, giving out its heat and cooling back into a liquid.
5. The refrigerant flows back into the expansion valve and the cycle repeat itself [17].

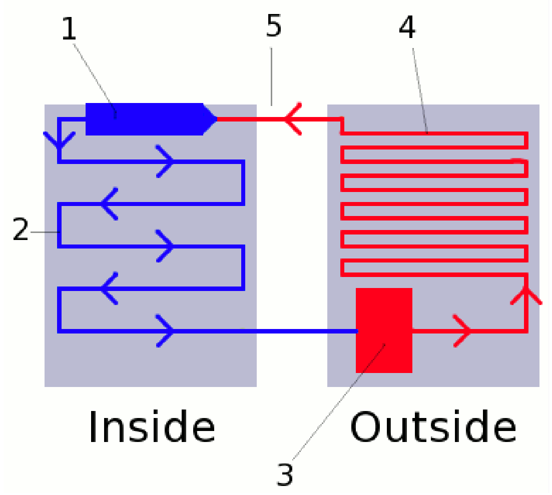

Figure II. 5 Refrigeration cycle [17]

The initial domestic refrigerators used mainly ammonia and sulfur dioxide as refrigerant. Some units used methyl chloride and methylene chloride. These refrigerants were replaced by CFC-12 in 1930s. In the beginning refrigerators were equipped with open type compressors driven by belt drive. In 1926 General Electric Company introduced the first refrigerator with a hermetic compressor. Soon after, the open type compressors were completely replaced by the hermetic compressors. First refrigerators used water-cooled condensers, which were then replaced by air cooled condensers. The domestic refrigerator based on absorption principle as proposed by Platen and Munters, was first made by Electrolux Company in 1931 in Sweden. In Japan the first mechanical domestic refrigerator was made in 1924. The first dual temperature (freezer-refrigerator) domestic refrigerator was introduced in 1939. The use of mechanical domestic refrigerators grew rapidly all over the world after the World War II. Today, domestic refrigerators are essential kitchen appliances. Except very few almost all the present day domestic refrigerators are mechanical refrigerators that use a hermetic compressor and an air cooled condenser. The modern refrigerators use either HFC-134a (hydrofluorocarbon) or isobutane as refrigerant [13].

II.2.3 Thermal Insulation

The aim of insulation in refrigerators is to keep heat outside. Refrigerators may have many different types of insulation. The insulator may be vacuum, styrofoam or a type of fiberglass. The insulation lies between the inner and outer walls of the refrigerator (Figure II. 6) [18].

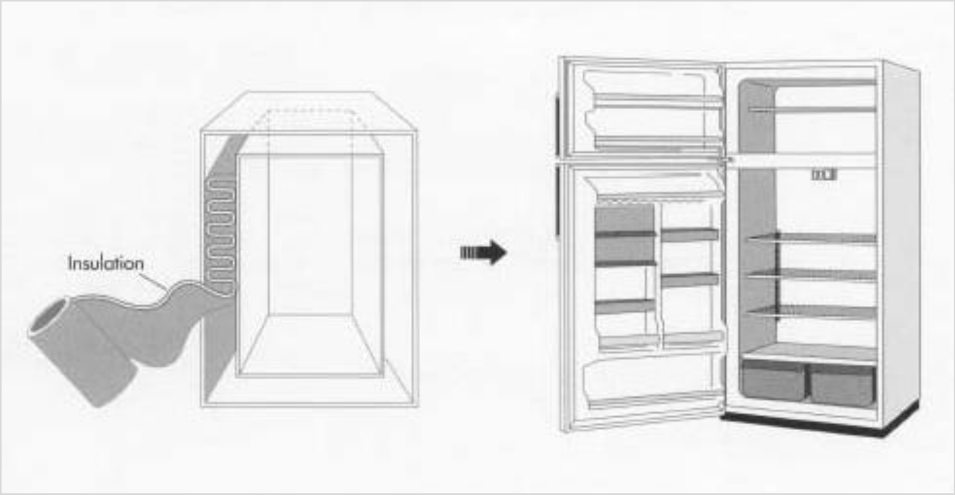

Figure II. 6 Insulation foam in refrigerators [19]

Heat travels through the movement of atoms in a substance. When there is greater space between atoms, heat has a harder time getting through the substance. Of course, there are other factors in heat transfer. However, the space between the atoms in air is very large, which makes it very hard for the heat to transfer through the air. This means that the heat from the outside of the refrigerator has a hard time heating up the inside of the refrigerator. If it were not for insulation, refrigerators would have to use much more energy to keep their contents cool [18].

Major appliance manufacturers used fiberglass materials for insulation prior to rigid polyurethane (PUR) foam insulation. In the mid to late 1960's refrigerator manufacturers began to use polyurethane plastic foam as insulation. Polyurethane foams gained acceptance in the cabinets of refrigerators and freezers since they provided a dual benefit. One of the benefits is that the material gave structural rigidity to the appliance which enabled manufacturers to reduce the amount of steel needed for each unit. In addition, energy performance is enhanced due to the higher resistivity to heat transfer by the polyurethane foam when compared with fiberglass insulation [20].

The last use of glass fiber as insulation in the doors of refrigerators occurred around 1992. The reason the change took so long was due to the high cost to redesign and retool the refrigerator cabinet for the new insulation. This retooling has resulted in a larger interior in a refrigerator while retaining the same exterior dimensions. In addition the rigid nature of the foam insulation has allowed refrigerator designers to reduce the thickness of metal exterior and plastic interior "skins" [20].

II.2.3.1 Polyurethane (PU) Foam

Polyurethane was first developed by Prof. Otto Bayer, as a replacement for rubber, during the first years of World War II. During World War II, polyurethanes were mainly used in military and aerospace applications, as well as chemical and corrosion resistant coatings to protect metal, wood and masonry. By the end of the war, they were being widely used in consumer and industrial products, such as cushions, coatings, and thermal insulation applications [21, 22]. In the 1970s, there was a growth in the use of rigid polyurethane (PUR) foam thermal insulation in refrigerators and panel products and in spray applied foam as building insulation [21].

Today, polyurethanes exist in a variety of forms including flexible foams, rigid foams, chemical-resistant coatings, specialty adhesives and sealants, and elastomers. Rigid polyurethane foams are used as insulation for buildings, water heaters, refrigerated transport, and commercial and residential refrigeration. These foams are also used for flotation and for energy management. Flexible polyurethane foams are used as cushioning for carpet and in upholstered furniture, mattresses, and automobiles. They are also used for packaging. The term "polyurethane elastomers" includes such diverse products as thermoplastic polyurethane, cast elastomers and Reaction Injection Molded (RIM) products. These materials go into a wide variety of applications from footwear and skate wheels to machinery housings, to athletic tracks to electronic media [23]. Main categories of PU applications and product examples are given in Table II. 2.

Table II. 2 Main categories of PU applications [22]

PU Application	**Product**
Flexible slabs	Furniture, matrasses, automobiles, carpets
Flexible moulded forms	Automobile seatings, matrasses
Rigid foams	Refrigerators, insulation board
Solid elastomers	Elastomers, footwear, adhesives, medical
Reaction injection moulding (RIM)	Automobiles (bumpers, side panels)
Carpet backing	Carpets
Two-component applications	Casting, sealants

In 1995, flexible and rigid foams had a US market share of 48% and 28%, respectively. These were followed by around 8% for PU elastomers and around 16% for other applications. 30-35 % of the world total consumption at that time belonged to North America, while Western Europe had a share of approximately 40 %. The Far East and the rest of the world, on the other hand, counted for 25-30 % of the total consumption. The total worldwide PU consumption was approximately 6000 million tonnes for 1995, which corresponded to about 5% of the total plastics consumption [22].

Polyurethane foams are formed by a reaction of isocyanates (derived from petroleum sources) with polyols (long-chain alcohols derived from vegetable sources) in the presence of catalysts and other additives [22]. The typical polyurethane structure and the urethane bond from which the material derives its name are given in Figure II. 7 and Figure II. 8, respectively.

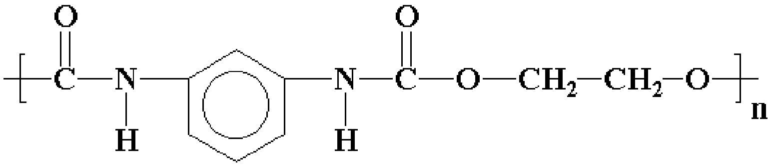

Figure II. 7 Chemical structure of typical polyurethane

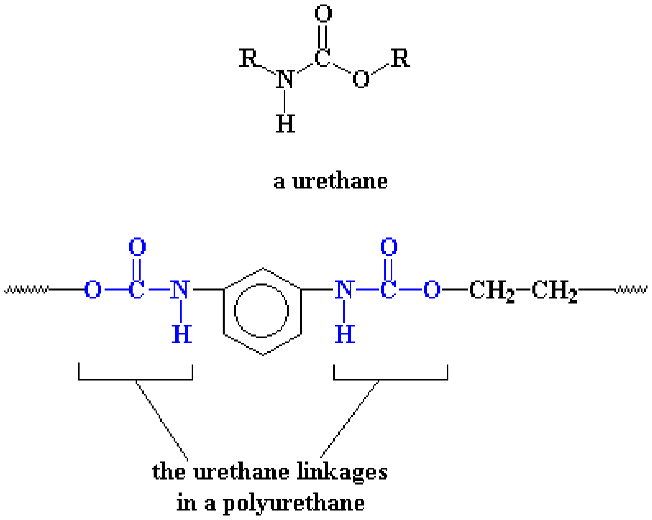

Figure II. 8 Urethane bonds in polyurethane [22]

Polyurethanes are composed of segments with the structure – (O-R'-O) – (CO-NH-R-NH-CO) – (O-R"-O) – (CO-NH-R-NH-CO) –, with organic groups R, R', R". They can be composed from:

1) a di-isocynate OCN-R-NCO like MDI (diphenylmethane di-isocyanate) or TDI (toluene di-isocynate)
2) a polyol (or polyether) or polyester HO-R'-OH such as polypropylene glycol (PPG) or polytetramethylene glycol (PTMG), or polycaprolactone (PCL) or polybutylene adipate (PBA)
3) small-molecule chain extenders (OH-R"-OH) like 1,4-butanediol (BDO) or 1,6-hexanediol (HDO)

Nevertheless, blowing agents are key components of a polyurethane formulation. They are needed to obtain the foam structure. Blowing agent is of great importance especially for rigid foams, affecting important properties such as thermal insulation, density and mechanical strength [24]. A wide range of polyurethane with different characteristics can be obtained from the mixture of polyols, isocyanates and blowing agent [22]. The final properties of polyurethane foam are directly related to:

- The isocyanate and polyol used in making foam
- The foam-making process itself
- The blowing agent used
- The resulting final density of the finished product [25]

Each of these features will influence the performance of particular polyurethane foam in a specific application. A classification can be made based on density and hardness, as shown in Figure II. 9.

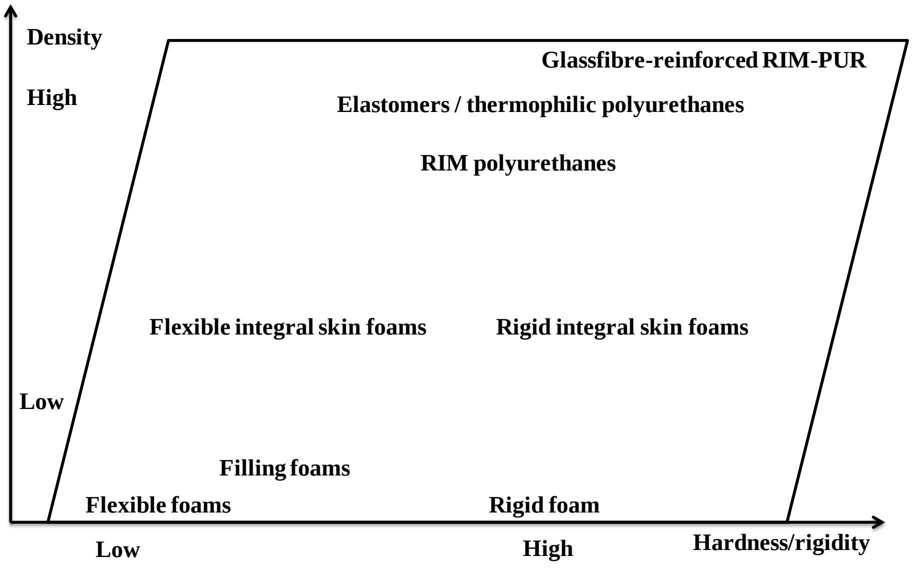

Figure II. 9 Characteristics of polyurethanes (density 20-1300 kg/m^3) [22]

Polyurethane foam can be categorized as closed cell and open cell foam (Figure II. 10). The closed cell foams are plastics where each bubble that creates the foam is continuous and completely spherical or oblong. Open cell foams, on the other hand, are plastics where the cell walls are incomplete and contain holes through which liquid and air can easily travel [22].

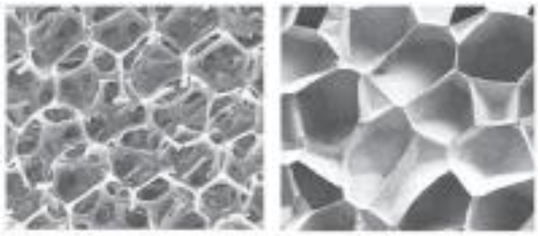

Figure II. 10 Open cell / Closed cell PU foam [22]

Rigid and flexible PU foams (PUR and PUF foams in short) can be classified according to their cell structure, which is either “open” or “closed”. Only a small amount of the cells are open in PUR foams and bulk densities are typically 30-35 kg/m^3. The blowing agent gas contained in the cells results in a very low thermal conductivity, and the main use of PUR foams is in insulating boards, refrigerators and freezers. Cross-section of PUR foam can be seen in Figure II. 11. PUF foams have almost a completely open cell structure with densities 20-45 kg/m^3. These materials are mainly found in mattresses, furniture and automobile seats [22].

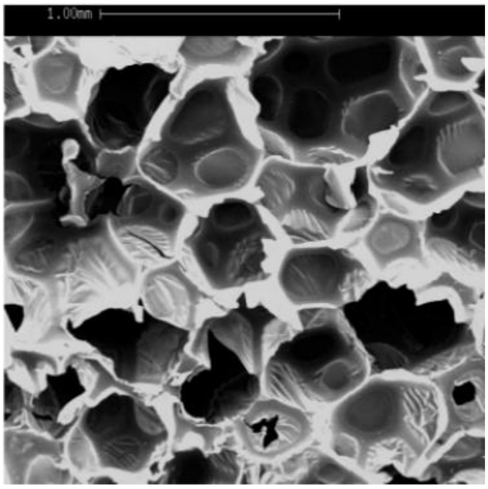

Figure II. 11 Scanning electron microscope (SEM) photo of commercial rigid PU [22]

II.2.3.2 Vacuum Insulation Panels (VIPs)

Vacuum insulation panels can be widely used in fridge, freezer, refrigerator, refrigerated containers. They offer very high thermal resistance in a very small space (Figure II. 12) [26].

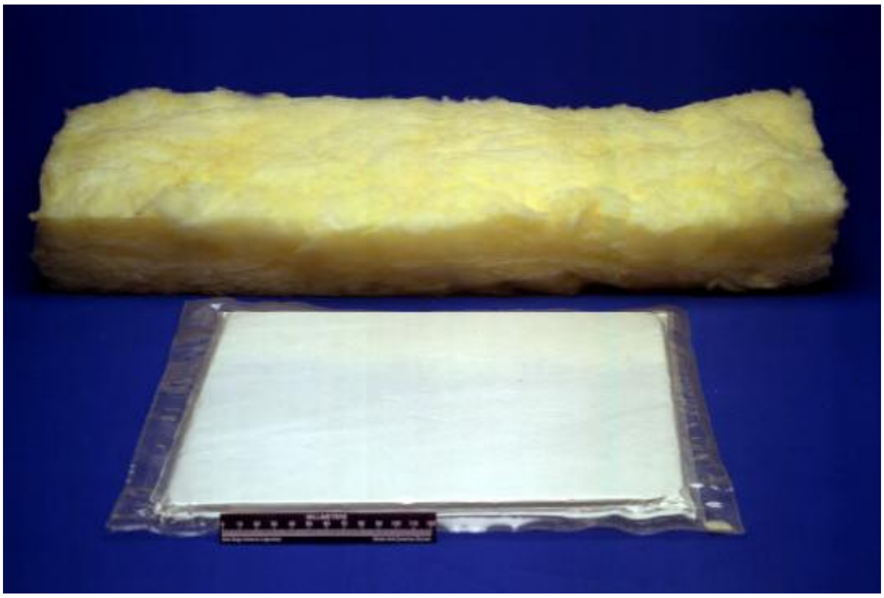

Figure II. 12 Comparison of thickness (Glass fiber insulation vs. VIPs) [26]

They provide extraordinary performance in reducing the total heat transfer across a space by eliminating convection, reducing radiation, and minimizing both solid and gaseous conduction. Thus, thermal conductivity can be greatly reduced.

Vacuum insulation panels offer very high thermal resistance in a very small space. There are mainly two main components, the core and the barrier (Figure II. 13) [26].

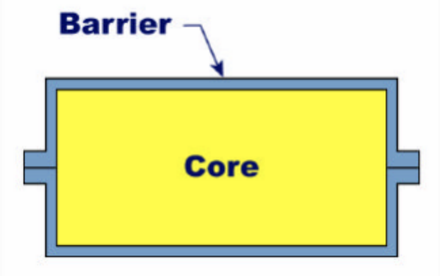

Figure II. 13 Main components of VIPs [26]

The core serve as support for the barrier material, it has low thermal conductivity and it must interfere with radiant heat transfer across the panel. The earliest vacuum panel concepts used powders as the core material and flexible plastic films as barrier materials. Soon it was discovered that if powdered filler is going to be used, some kind of inner porous container between the core and the barrier is also needed, so that powder would not be sucked into the vacuum system. The powders included fumed silica, opacified fumed silica, silica bag-house dust, perlite, precipitated silica, fly ash, clays and mixtures of these powders [26].

On the other hand, plastic laminates and metallic foils were used as barrier materials in the earliest concepts. The plastic laminates were easier to seal, but were more permeable. The metallic foils required brazed, soldered, or welded edges, but were capable of holding a much lower pressure for extended periods of time. Later generations used barriers that were multi-layer plastics and multi-layers films that incorporate both plastic and metallic elements. Later, materials that can absorb gases (getters), which find their way into the evacuated space, were developed [26].

II.3 CFC-11 AS BLOWING AGENT

CFC-11 has been extensively used before the ban (1980-1996) to blow polyurethane (PUR) foams for insulation. The blown PUR forms rigid, closed cell foams containing CFC-11 gas in tiny gas bubbles. The bubbles are maintained in the foam after hardening of the PUR. The CFC is a low heat conductivity gas adding to the insulation properties of the foam. At the same time the loss of CFC from the foam due to diffusion is very low [27].

Rigid polyurethane foams are produced by injecting blowing agent into a mixture of polyols and isocyanates, thus creating the bubbles that provide the insulating capabilities of the material. Low-boiling organic liquids were found to produce better results, with the additional benefit of improving the insulating properties of the foam [28]. The most frequently used blowing agent for insulating properties has been trichlorofluoromethane (CFC-11) [22].

CFCs have provided the following [29]:

- Lower thermal conductivity than other blowing agent alternatives
- Stable thermal conductivity performance with time
- Ease of processing (suitable boiling points, non-flammability, low toxicity etc.)
- Good product properties (fire performance, dimensional stability, strength etc.)

Thermal conductivity of CFC-11 and its replacements can be seen in Figure II. 14.

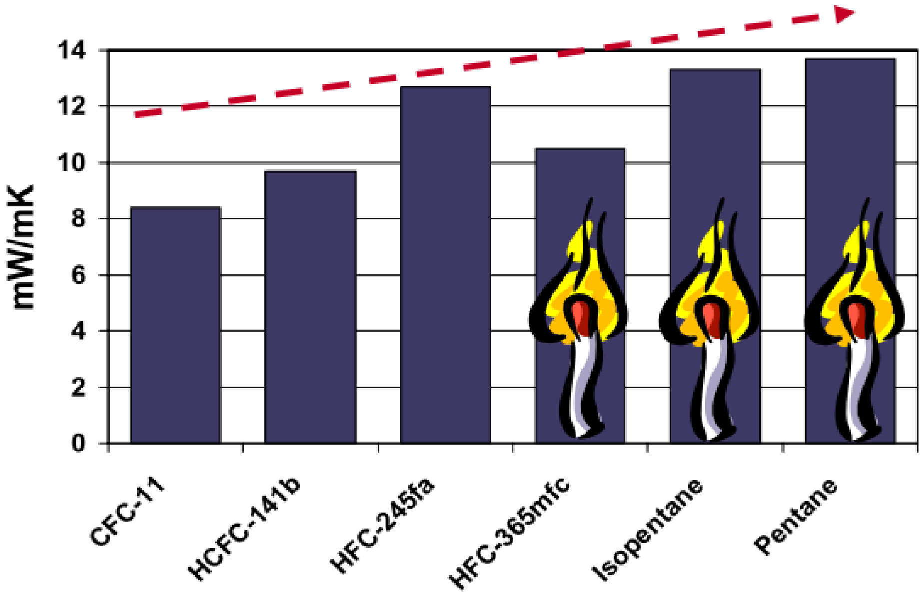

Figure II. 14 Thermal conductivity (mW/mK) of CFC-11 and other blowing agents [30]

II.3.1 Effects on Ozone Layer

Ozone layer is a concentration of ozone gas about 25 miles above the surface of the earth, that keeps out harmful ultraviolet light and plays an important role in regulating the earth's climate [31].

Stratospheric ozone is damaged by long-lived chlorinated, brominated and fluorinated hydrocarbons. Of particular relevance in this regard are the chlorofluorocarbons (CFC) [32]. CFC based coolants had the risk of being released to the atmosphere accidentally during production, through damages to the cooling system during use, accidentally or on purpose during service, and most likely upon disposal [31]. CFCs are a group of aliphatic organic compounds containing the elements carbon and fluorine, and other halogens (especially chlorine) and hydrogen [33]. Trichlorofluoromethane or CFC-11 (CCl_3F) is a compound with one fluorine (F) and three chlorine (Cl) atoms attached to one central carbon [34]. Figure II. 15 shows the molecular structure of CFC-11.

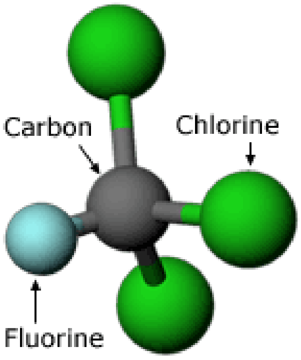

Figure II. 15 Molecular structure of trichlorofluoromethane (CFC-11) [35]

When CFC-11 is released into the atmosphere, it slowly rises into the stratosphere [31]. In the stratosphere, UV radiation breaks off chlorine atoms from the CFC molecule. The chlorine atom then attacks ozone molecule (O_3), breaking it apart and destroying the ozone. The resulting molecules are ordinary oxygen molecule (O_2) and chlorine monoxide molecule (ClO). The chlorine monoxide molecule (ClO) is attacked by a free oxygen atom releasing the chlorine atom and forming an ordinary oxygen molecule (O_2). The free chlorine atom then combines with another ozone molecule (O_3). One chlorine atom can repeat this destructive cycle thousands of times [36]. Figure II. 16 demonstrates the effects of CFC-11 on the ozone layer.

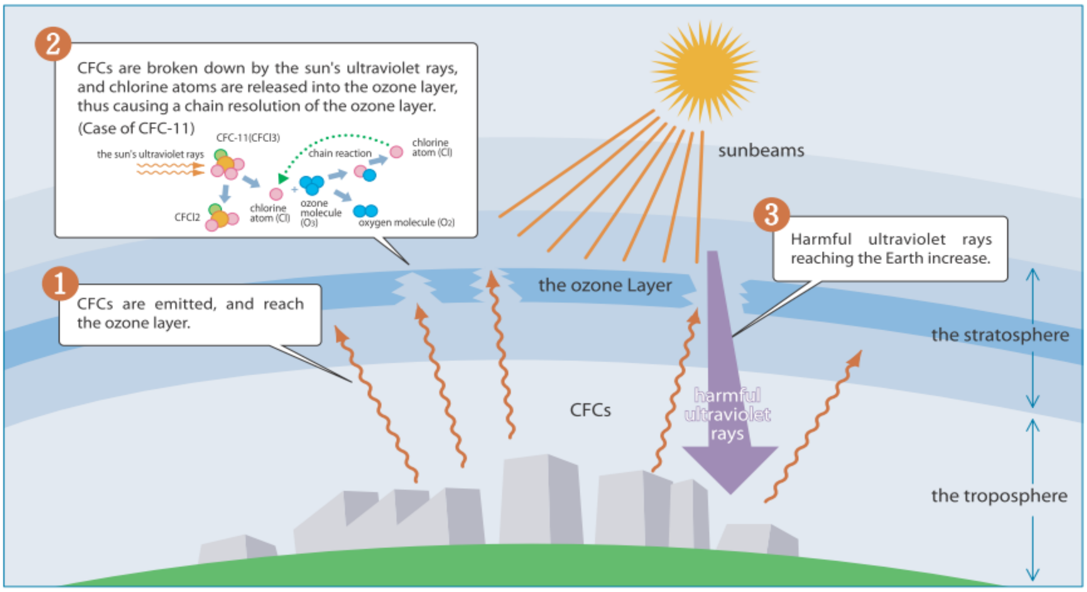

Figure II. 16 The mechanism of the ozone layer depleted by ozone depleting substances [28]

Increased ozone depletion is accompanied by an increase in UV-B radiation at the surface of the earth, as the stratospheric ozone layer filters out a large part of the

UV-B radiation. An increase in UV-B radiation at the earth's surface can lead to a greater incidence of skin and eye disease in humans and can impair the human immune system. Even a relatively small increase in the average UV-B radiation flux is expected to cause damage to ecosystems and to have a long-term influence on the food chain [32].

The adverse effects of CFCs on the ozone layer were recognized during the 1970s. With the discovery of the Antarctic ozone hole in 1985 there was a global act to control chlorofluorocarbons (CFCs) and other ozone-destroying chemicals [37]. In September 1987, the Montreal Protocol on Substances That Deplete the Ozone Layer was signed by 25 nations and the European Community. The Protocol was the first international environmental agreement. The Protocol called for a requirement to reduce the production of CFCs by 50% by 1999. However, new scientific evidence surfaced after the entry into force of the Protocol, indicating that ozone depletion was more serious than originally thought. Accordingly, in 1990 (London), 1992 (Copenhagen), and 1995 (Vienna), amendments were made to the Protocol to regulate the phase-out of the original chemicals and the control and phase-out of additional chemicals. The principal provisions of the Montreal Protocol as it now stands are as follows:

- Production of CFCs, halons, methyl chloroform ceased at the end of 1995 in industrial countries and will be terminated by 2010 in developing countries. Developing countries are defined in the Protocol as those that use less than 0.3 kilograms (kg) of ODS per capita per year.
- HCFCs, originally developed as a less harmful class of CFC alternatives, will be phased out by 2020 in industrial countries, with some provisions for servicing equipment to 2030. Developing countries are to end consumption by 2016 (base year 2015) and phase out use by 2040 [37].

The regional variation in phase-out is shown in Figure II. 17.

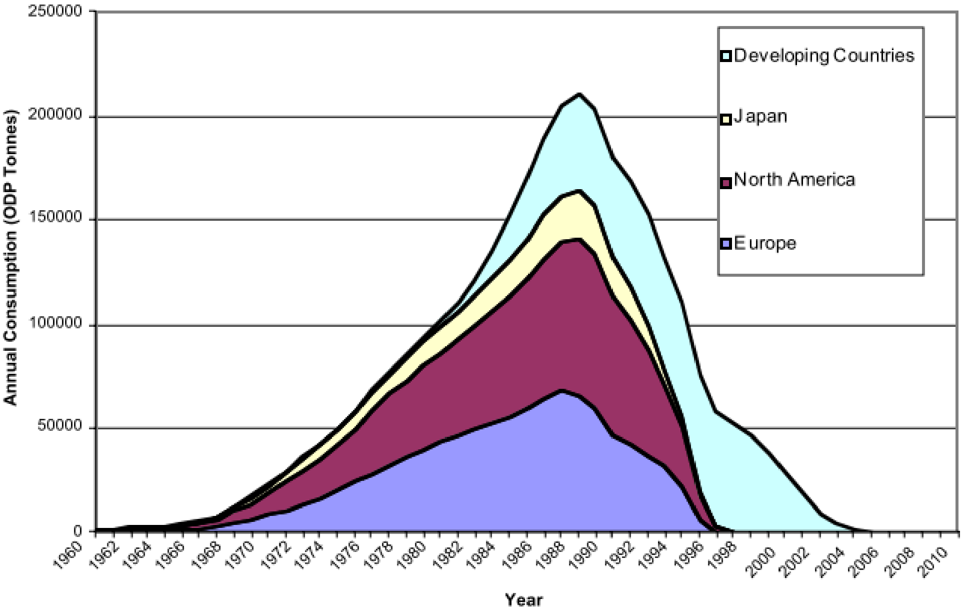

Figure II. 17 Phase-out of CFC blowing agents in rigid foams [29]

II.3.2 Ozone Depleting Potential (ODP)

The measure of a substance's potential impact on the Earth's ozone layer is expressed in terms of its Ozone Depletion Potential (ODP). This calculation is based on the amount of ozone destroyed by steady state emissions of a gas compared to that destroyed by the emissions of the same amount of CFC-11. The ODP represents the number of chlorine or bromine atoms in a substance and their lifetime after being released. The accepted ODP calculation is as follows [38]:

$$\text{ODP} = \frac{\text{Globally averaged ozone depletion due to "X"}}{\text{Globally averaged ozone depletion due to CFC-11}}$$

CFC-11 became the reference ozone depleting substance (ODS), with ozone depleting potential (ODP) = 1. Table II. 3 shows ODP values of various gases.

Table II. 3 Ozone depletion potential of main ozone depleting substances [37]

ODS	**ODP**
CFC-11	1.0
CFC-12	1.0
CFC-113	0.8
HCFC-11	0.05
HCFC-123	0.02
HCFC-124	0.02
HCFC-141b	0.15

Table II. 4 (continued) Ozone depletion potential of main ozone depleting substances [37]

ODS	**ODP**
HCFC-142b	0.06
HCFC-225ca	0.01
HCFC-225cb	0.04

ODSs are nowadays classified in two classes (class I and less harmful class II). Class I includes the fully halogenated CFCs, halons, and the ODSs that are the most threatening to the ozone layer. In general, Class I substances cause greater environmental harm than Class II substances. Class II compounds are those substances that are known or reasonably anticipated to have harmful effects on the stratospheric ozone layer. Class II substances are hydrochlorofluorocarbons (HCFC) [39].

II.3.3 Replacements

Before 1993, the most widely used blowing agent used was trichlorofluoromethane (CFC-11), which has been phased out due to its ozone depleting effect after release into the atmosphere [40]. The decision for phase out of CFCs under Montreal protocol resulted in adopting more suitable alternative foam blowing agents. Among the new blowing agents being developed, compounds with no ODP and minimal GWP are the most environmentally desirable. Besides ecological consideration, thermal conductivity of PU foam with different blowing agents is an important factor. Increase of thermal conductivity will either decrease energy efficiency or will force manufacturers either to increase the insulation thickness which will reduce the usable net volume [41]. The considerations in the evaluations of alternative blowing agents also include safety (toxicity and flammability), cost and availability, and regulatory requirements [42].

Since the ban, household refrigerators have transitioned from chlorofluorocarbons (CFCs), to low or non-ozone depleting compounds such as hydrochlorofluorocarbons (HCFCs), and then to hydrofluorocarbons (HFCs) and hydrocarbons (HCs). Many manufaturers initially used HCFC-141b as blowing agent and HFC-134a as refrigerant, although some countries have opted for isobutane as refrigerant and cyclopentane as blowing agent options [43]. Hydrochlorofluorocarbons (HCFCs) such as HCFC-141b ($C_2H_3FCl_2$) was used widely as a substitute for CFC-11, but by 2005 use of HCFC-141b was also banned in most developed countries because of recognition of its ozone depletion potential. Instead, hydrofluorocarbons (HFCs) such as HFC-134a (CH_2FCF_3) or HFC-245fa ($CF_3CH_2CHF_2$) are used extensively. However, HFCs released to the atmosphere are potential greenhouse gases that may contribute significantly to global warming [40]. On the other hand, vacuum panels may be used in the future [42]. Properties of some of the alternative blowing agents are given in Table II. 5.

Table II. 5 Zero ODP and Zero ODP/Low GWP Blowing agents [44, 45]

Compound	**MW**	**Boiling Point (°C)**	**Thermal Conductivity 25°C (mW/mK)**	**ODP**	**GWP**
HCFC-141b	117	32	--	0.12	725
HFC-134a	102	-27	--	0	1300
HFC-245fa	134	15	12	0	820
HFC-365mfc	148	40	12	0	840
Cyclopentane	70	49	13	0	0
Isopentane	72	28	14	0	11

II.4 RECYCLING OF END-OF-LIFE REFRIGERATORS

An average domestic refrigerator weighs 36 kg with a composition of 63% iron, 12% plastics, 11% polyurethane, 5% aluminum, 2.5% copper, 2% glass, 1.7% (oil and CFC-12) and 2% other (Figure II. 18) [46].

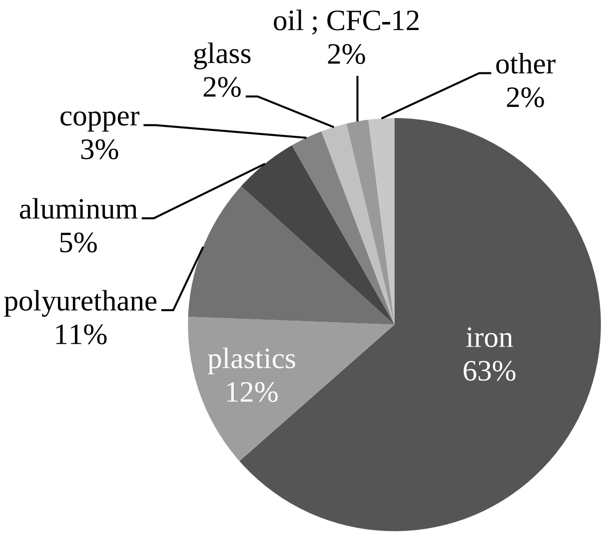

Figure II. 18 Composition of a typical refrigerator [46]

Household appliances are shredded after their useful lives in order to recycle the high content of metals. The recycling activities are carried out in shredders that recover the metals and produce a waste residue consisting primarily of plastics, rigid insulation foams, electrical wires and other non-magnetic metal pieces. The shredder waste is disposed of in mixed waste landfills in most countries [47]. However, refrigerators, along with other white goods (large domestic appliances) are not typical household wastes due to their bulky nature and hazardous components, particularly their ozone depleting substances (ODS) contained within [48].

A refrigerator with polyurethane insulation foam, blown with CFC-11, contains approximately 520 g of CFC-11 [47]. First-year release rate of the CFC contained in the insulation foam is 6%. During the lifetime of a refrigerator, the annual release rate drops to 0.25% (Table II. 6). As seen in Table, 15-year-old refrigerator still contains 90% of the BA [29].

Table II. 6 Release of CFC-11 from PU foam [29]

Foam Type	**First year release (%)**	**Release Rate (%/yr)**	**Time to Total Release (years)**	**Lifetime of Foam (years)**	**Total remaining at decommissioning (%)**
PU-Refrigerator	6	0.25	376	15	90

In order to process polyurethane foam insulation from appliances, it is first necessary to separate the foam by removing the steel skins and plastic liners that surround the insulation. The standard practice has been to mechanically saw the appliance boxes into panels and then separate the steel and plastic components using hand tools. This disassembly technique releases some CFC-11 into the atmosphere due to the breakage of the insulation during the removal. However, the amounts of release caused in this manner are not quantified. Once the foam has been separated from its surroundings, the processing can begin [38].

The foam can be delivered to an incinerator where it is added to the fuel mix. However, the incineration of foam as a means of destroying the CFCs has proven to be problematic. A sampling of incinerator emissions in Germany revealed the presence of dioxin, phosgene and nitric oxides in addition to measurable quantities of CFC-11 that remained undestroyed by the incineration process. The highly corrosive nature of the foam insulation due to the presence of chlorine products were found to be potentially damaging to the incinerator facilities. The policy of a large operator of cement kilns in the United States echoes this concern, While the facilities do accept organic waste products such as paint thinners, inks and some industrial cleaning solvents, high chlorine content fuels such as polyurethane foam insulation are not acceptable for use as fuels in the manufacture of cement [38].

II.4.1 Legislations in EU relevant to end-of-life refrigerators

EU legislation restricting the use of hazardous substances in electrical and electronic equipment (Directive 2002/95/EC) and promoting the collection and recycling of such equipment (Directive 2002/96/EC) has been in force since February 2003. The objective of this legislation is to increase the recycling and/or reuse of such products. It also requires heavy metals such as lead, mercury, cadmium, and hexavalent chromium and flame retardants such as polybrominated biphenyls (PBB) or polybrominated diphenyl ethers (PBDE) to be substituted by safer alternatives.

Despite such rules on collection and recycling only one third of electrical and electronic waste in the European Union is reported as separately collected and appropriately treated. A part of the other two thirds is potentially still going to landfills and to sub-standard treatment sites in or outside the European Union. The collection target of 4 kg per person per year does not properly reflect the amount of WEEE arising in individual Member States. Illegal trade of electrical and electronic waste to non-EU countries continues to be identified at EU borders.

Inadequately treated e-waste poses environmental and health risks. In December 2008, the European Commission therefore proposed to revise the directives on electrical and electronic equipment in order to tackle the fast increasing waste stream of such products. The aim is to increase the amount of e-waste that is appropriately treated and to reduce the volume that goes to disposal. The proposals also aim to reduce administrative burdens and ensure coherency with newer policies and legislation covering, for example, chemicals and the new legislative framework for the marketing of products in the European Union.

The Commission proposes to set mandatory collection targets equal to 65% of the average weight of electrical and electronic equipment placed on the market over the two previous years in each Member State. The recycling and recovery targets of such equipment would cover the re-use of whole appliances and weight-base targets would increase by 5%. Targets are proposed also for the recovery of medical devices [49].

II.4.2 Current Situation in Turkey

In Turkey, the draft of “Waste Electrical and Electronic Equipment Control Regulation” (AEEE Kontrolü Yönetmeliği) has been prepared in accordance with the EU legislation and is expected to enter into force in the near future. According to the draft, electrical and electronic equipments are classified into ten categories. Refrigerators fall under the category of large domestic appliances. Materials and components to be selectively removed include CFCs, HCFCs, HFCs and HCs. Moreover, refrigerator recycling facilities will be responsible for the storage of polyurethane foams separately. In addition, the fourth clause of the draft refers to the “Directive on Ozone Depleting Substances” (Official Gazette No. 27052, dated 12.11.2008) for the regulation of chlorofluorocarbons (CFCs) [50]. Besides, hazardous wastes are also under regulation with “The Turkish Regulation for General Principles of Waste Management” (Official Gazette No.26927, dated 05.07.2008). The hazardous waste categories and waste codes are given in Annex IV (Waste Categories) of the regulation which is in line with European Waste Catalogue [50]. Waste codes and definitions relevant to refrigerator disposal are given in Table.

Table II. 7 Waste codes and definitions for end-of-life refrigerators [51]

Waste Code	**Definition**
16 02	Wastes from Electrical and Electronic Equipment
16 02 11	Discarded equipment containing chlorofluorocarbons, HCFC, HFC
20 01	Municipal Wastes (Household Waste and Similar Commercial, Industrial and Institutional Wastes) including Separately Collected Fractions
20 01 23	Discarded equipment containing chlorofluorocarbons

CHAPTER III

THE STUDY

III.1 DETERMINING THE NUMBER OF REFRIGERATORS CONTAINING POLYURETHANE FOAM BLOWN WITH CFC-11

The blowing agent used in rigid polyurethane foams for the insulation of refrigerators in Turkey was CFC-11 until 1995. Since the lifetime of a refrigerator ranges from 15 to 40 years, it is expected that there will be significant amounts of refrigerators to be disposed of in the near future. As a result, these end-of-life refrigerators will result in release of significant amount of CFC-11 to atmosphere. However, there is limited information on the amounts of refrigerators that are to be disposed of in the near future. In order to determine the amount of refrigerators containing polyurethane foam blown with CFC-11, sales data of household appliances are obtained from TURKBESD. In addition, average lifetime of refrigerators was gathered from a study based in Canada [52]. A survey was conducted to evaluate the retirement ages and replacement frequency of refrigerators. With the help of the model obtained from the Canadian study, the amount refrigerators containing CFC-11 which is still-in-use in Turkey was determined. The model was used to obtain the percentage of the refrigerators that were purchased between 1986 and 1995 and are still used in households.

III.2 DETERMINING THE AMOUNT OF CFC-11 IN REFRIGERATORS IN TURKEY

Studies have documented that during the lifetime of an appliance, very little blowing agent is released to the atmosphere which was related to the encapsulation of polyurethane foam by the appliance walls and minimal air movement through the foam. However, information on the amount of CFC-11 remaining in end-of-life refrigerators is scarce. To determine the amount of CFC-11 remaining in end-of-life refrigerators, foam samples were taken from an end-of-life refrigerator produced prior to 1995 and analyzed for CFC-11.

III.2.1 Polyurethane Foam Sampling

Polyurethane samples were taken from a refrigerator produced in 1993 with rigid polyurethane foam containing CFC-11 as blowing agent. Foam panels were obtained from the unit by first drilling a hole and then cutting the panel to desired sizes using a saw (Figure III. 1).

Figure III. 1 Sampling from foam panel using reciprocating saw

Foam panels were cut off from the top, bottom, left and right sides, rear and the door, leaving the plastic casing and metal exterior of the refrigerator units attached to the foam (Figure III. 2).

Figure III. 2 Foam sampling from refrigerator

Photographs in Figure III. 1 and Figure III. 3 show how the panels are cut off and removed from refrigerator unit. Two panels (15 × 15 cm) were cut off from top, bottom and door. Other four panels were cut off from the rear, right and left sides; two of them were from the freezer part while the other two were from the refrigerator part of the unit.

Figure III. 3 Cutting of foam panels into desired sizes (15×15 cm) after removal from the unit

Following the removal of the panel from the unit, the edges of the core samples were sealed with aluminum tape to prevent the escape of CFC-11 (Figure III. 4). Taped foams are placed in Tedlar bags and sealed (Figure III. 5). At the laboratory, the panels were stored in refrigerator prior to analysis.

Figure III. 4 Wrapping of samples with aluminum tape

Figure III. 5 Placing foam panels in Tedlar bags

III.2.2 Measurement of BA Content in Foam Panels

Foam samples with 1-cm diameter were cut out from the center of the panels with a cork borer (Figure III. 6) after removing the plastic casing and metal exterior attached to the foam. Three 1-cm diameter foam samples were cut out from each panel and weighed. Each sample was then placed in 1-L (exact capacity: 1127 mL) glass bottles. Bottles were then sealed with PTFE-lined silicon septa and screw caps with aperture. When sampling the foam using the cork bore, BA was released from both the cutout foam and from the surrounding foam mass. To quantify this release, the foam sampling was carried out in a sealed glove bag, from where air samples were taken to be measured for BA by gas chromatographic analysis. Foam sampling was carried out in a sealed glove bag, since CFC-11 would be released while the polyurethane foam is cut out from the panel with cork borer. A photograph of glove bag taken during sampling is given in Figure III. 7.

Figure III. 6 Cork borer

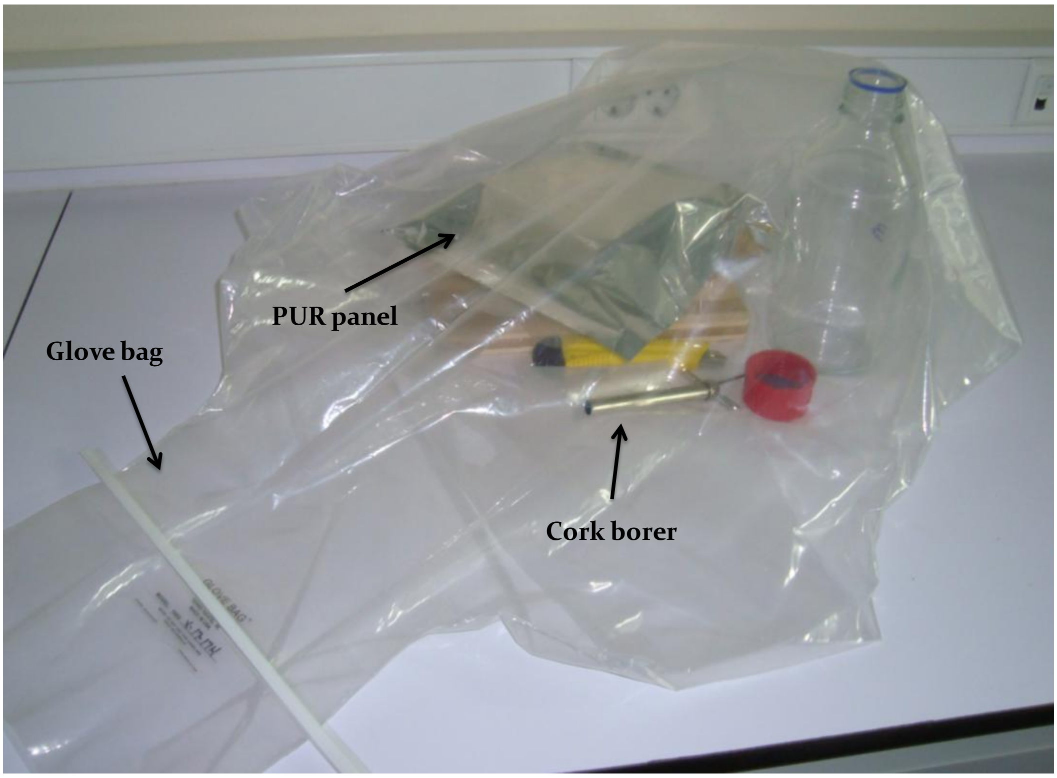

Figure III. 7 Sampling in glove bag

Polyurethane panel, cork borer, a knife to remove the plastic and metal casing from the foam, and 1-L glass bottles with caps (Figure III. 8) are placed in glove bag. To determine the amount of CFC-11 released during sampling, a 500-mL (exact capacity: 630-mL) glass bottle was also put in the glove bag and capped before the glove bag is opened after sampling (Figure III. 9).

Figure III. 8 1L glass bottle with foam sample

Figure III. 9 Core foam sampling in glove bag

In order to extract CFC-11 from the PUR foam samples, a heating method was applied. 1-L glass bottles with PU samples were incubated in an oven for 48 hr at 140°C (Figure III. 10).

Figure III. 10 Incubation at 140^{o}C

Gas samples were drawn from the headspace and injected to a gas chromatography (GC) coupled with a mass spectrometer (MS) after being cooled down to room temperature.

III.2.3 Gas Chromatography-Mass Spectroscopy (GCMS) Analysis

Analysis of CFC-11 was performed on a Shimadzu QP-2010 Plus EI gas chromatograph mass spectrometer (Figure III. 11). The gas samples were injected manually as direct on-column injections on a generating station - CarbonPlot column (30 m × 0.32 mm × 1.50 µm; Agilent J&W Scientific Inc.) with helium as carrier gas.

CFC-11 was analyzed with an isothermal column temperature of 180°C. The carrier gas flow was set at 2.15 mL/min, and a sample split of 1:3 was used. Injection volume of samples was 50 µL throughout the project period.

Figure III. 11 Gas chromatograph-Mass spectrometer

CFC-11 was detected and quantitated based on the compound specific mass / charge (m/z ions) ions (101) and a retention time of approximately 5 minutes.

Calibration curve was constructed by injection of a liquid CFC-11 standard dissolved in cyclohexane (Dr. Ehrenstorfer) at four different concentration levels. Concentration of the liquid standard was 10 ng / µL. Volumes of 1.5 µL, 2 µL, 3 µL and 4 µL was injected to GCMS for calibration. Calibration curve was obtained for a mass range of 15 to 40 ng. The calibration curve is given in Figure III. 12.

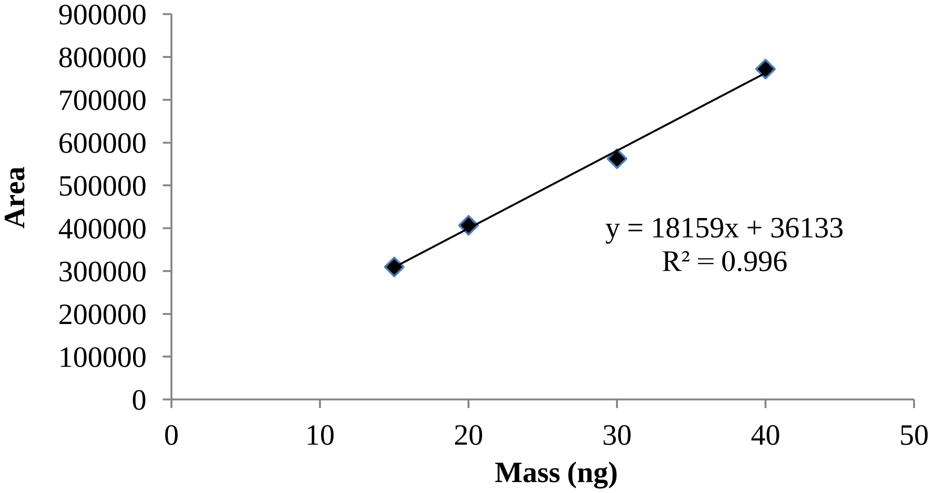

Figure III. 12 Calibration Curve for CFC-11 analysis

CHAPTER IV

RESULTS & DISCUSSIONS

IV.1 THE AMOUNT OF REFRIGERATORS CONTAINING POLYURETHANE FOAM BLOWN WITH CFC-11

To determine the amount of refrigerators containing polyurethane foam blown with CFC-11, total amounts of production, export, import and domestic sales data for refrigerators was obtained from Turkish Association of Household Appliances Manufacturers (TURKBESD) (Figure IV. 1).

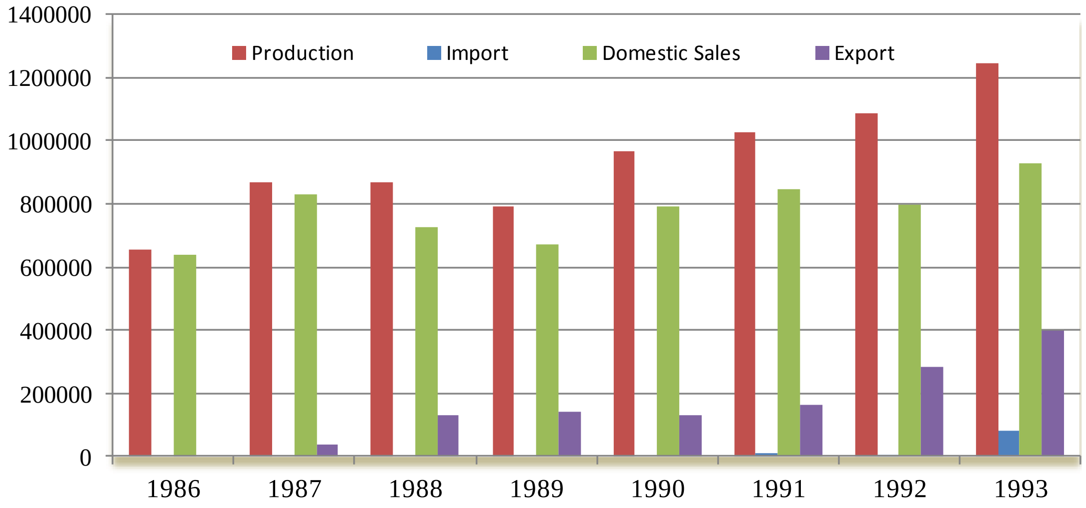

Figure IV. 1 Production, import, export and domestic sales data of refrigerators (1986-1995)

As given in Table IV. 1, the total number of domestic sales was approximately 7 million between years 1986 and 1995. Domestic sale numbers before 1986 were not available; therefore it is not included in this study. Data on frequency of refrigerator replacement was attained from a survey conducted in Canada [52]. Non-linear regression analysis was done by Sigma Plot 11.0 (Systat Software Inc.) to obtain the curve for the rate of refrigerator with respect to its age demonstrated in Figure IV. 2.

Table IV. 1 Production and sales data of refrigerators between 1986-1995

Year	Production	Import	Export	Domestic sales
1986	654 732	-	-	637 513
1987	870 393	-	39 760	830 633
1988	868 015	-	130 737	728 162
1989	793 121	-	142 144	669 934
1990	965 087	-	132 156	792 899
1991	1 026 075	9374	160 394	848 656
1992	1 087 416	3281	281 898	796 715
1993	1 247 016	83 619	396 801	927 180
1994	1 265 135	37 883	585 973	767 267
TOTAL	**8 776 990**	**134 157**	**1 869 863**	**6 998 959**

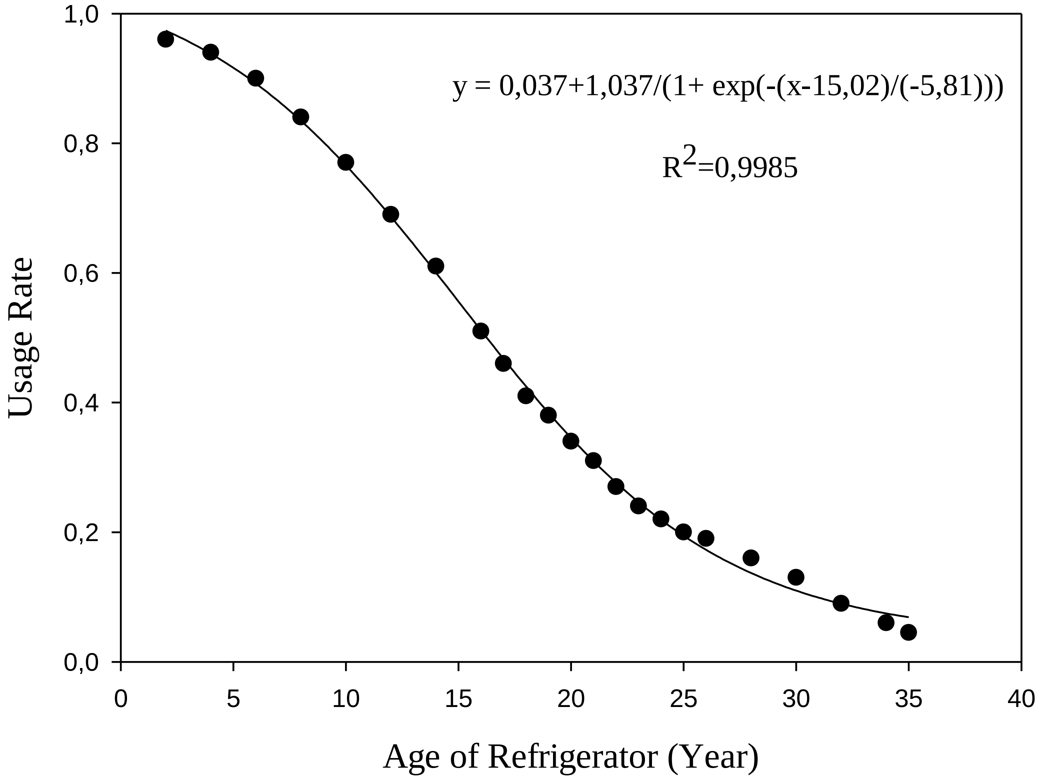

Figure IV. 2 Survival curve for refrigerators with respect to refrigerator age

Amount of refrigerators (sold between 1986 and 1995) which are still-in-use were determined with the survival function obtained from the non-regression analysis.

It is obtained that the amount of refrigerators sold between 1986 and 1995, and that are still in use ranges from 20% to 46%, as demonstrated in Table IV. 2. This indicates that of the 7 million refrigerators sold domestically from 1986 to 1995 in Turkey; 2.24 million are still in use.

Table IV. 2 Refrigerators produced between 1986-1995 and still-in-use

Production Year	Refrigerators still in use (%)	Amount of refrigerators still in use
1986	20	127 503
1987	22	182 739
1988	24	174 759
1989	27	180 882
1990	31	245 799
1991	34	288 543
1992	38	302 752
1993	41	380 144
1994	46	352 943
TOTAL		**2 236 063**

A study reported that a refrigerator contains 4000 g polyurethane foam and 520 g CFC-11 [46]. According to these data, total amount of polyurethane foam that would be disposed of with 2.24 million refrigerators was determined. The values calculated for the refrigerators manufactured between 1986 and 1995 are given in Table IV. 3. It is found that 8944 tons of polyurethane foam has to be managed along with the disposal of end-of life refrigerators in the near future.

Table IV. 3 Amount of polyurethane in refrigerators manufactured between 1986 and 1995 and still in use

Production Year	Amount of refrigerators still in use	Amount of PU, ton
1986	127 503	510
1987	182 739	731

Table IV. 4 (continued) Amount of polyurethane in refrigerators manufactured between 1986 and 1995 and still in use

Production Year	Amount of refrigerators still in use	Amount of PU, ton
1988	174 759	699
1989	180 882	724
1990	245 799	983
1991	288 543	1154
1992	302 752	1211
1993	380 144	1521
1994	352 943	1412
TOTAL		**8944**

Previous studies have documented that during the life of an appliance, very little BA is released to the atmosphere. This is primarily because the foam is encapsulated by the appliance walls and there is minimal air movement through the foam [41]. A report stated that the release of CFC-11 from refrigerators in the first year is 6% and 0.25% / year in the following years [29]. It is stated that the retention within domestic appliances is particularly high because of the metal/plastic encapsulation of the foam. These retention levels have been verified by the appliance industry through cross checks on 25 year-old units blown with CFC-11 [29]. This implies that total release of CFC-11 from a refrigerator will take 377 years. In other words, if a 15-year-old refrigerator is disposed and shredded, the amount of CFC-11 still retained in the unit will be 90% or 470 g. For a 25-year-old refrigerator, on the other hand, this amount drops to 88% or 458 g.

These results show that considerable amounts of CFC-11 will be released from polyurethane foams used in refrigerators once they reach their end of life and will be disposed for recycling. Amounts of CFC-11 retained in refrigerators with respect to refrigerator age were calculated and given in Table IV. 5. First of all, percentage of CFC-11 remaining in refrigerators were calculated given that the first year release is 6% and 0.25% in following years. It was determined that the amount varied between 88% to 90% for refrigerators produced and sold from 1986 to 1995. These values are then multiplied with the amount of refrigerators that are expected to be still in use (Table IV. 2).

It was found that the amount of CFC-11 that is expected to be released with the disposal and recycling of 2.24 million end-of-life refrigerators will be 1037.3 tons.

Table IV. 5 Amount of CFC-11 remaining in refrigerators manufactured between 1986 and 1995

Production Year	**Amount of refrigerators still in use**	**CFC-11 remaining in PU, %**	**CFC-11 remaining in PU, ton**
1986	127 503	88,00%	58,3
1987	182 739	88,25%	83,9
1988	174 759	88,50%	80,4
1989	180 882	88,75%	83,5
1990	245 799	89,00%	113,8
1991	288 543	89,25%	133,9
1992	302 752	89,50%	140,9
1993	380 144	89,75%	177,4
1994	352 943	90,00%	165,2
TOTAL			**1037,3**

Since one ton of CFC-11 is capable of depleting one ton of ozone, ozone depletion potential of refrigerator insulation foams will be 1037 ton. Considering that aforementioned refrigerators are going to be discarded according to Waste Electrical and Electronic Equipment legislation, precautions must be taken immediately in Turkey for the proper disposal of polyurethane insulation foam containing CFC-11.

IV.2 THE AMOUNT OF CFC-11 IN REFRIGERATORS IN TURKEY

To quantify the amount of CFC-11 remaining in end-of-life refrigerators, foam samples were taken from an obsolete refrigerator produced in 1993 and having polyurethane foam blown with CFC-11. At least two core foam samples were taken from each panels. These samples were incubated in closed glass bottles at 140^{o}C for 48 hours to extract the CFC-11 retained within the foam. The CFC-11 gas released from the foam samples during incubation was analyzed with a GC/MS. Results given in the following sections are the average values of four 50-μL injections.

IV.2.1 Effects of Temperature on CFC-11 Release

It was reported that heating of the samples accelerates the release of CFC-11 from the foam [41]. To evaluate the effect of temperature and incubation duration on the release of CFC-11 from the polyurethane, two core foam samples were taken from the left-side of the refrigerator unit and incubated for 24 hours at 100°C instead of for 48 hours and 140°C (Figure IV. 3).

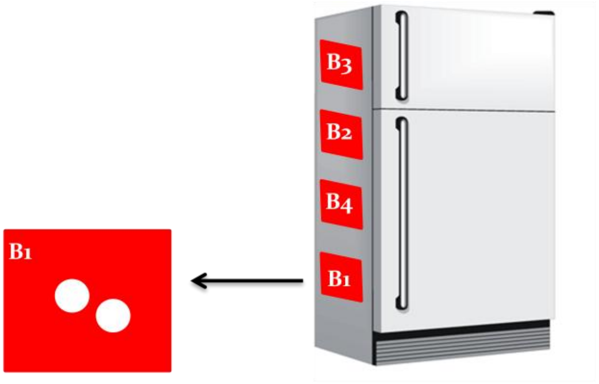

Figure IV. 3 Sampling from left side of the refrigerator

The results of this experiment are demonstrated in Table IV. 6. The average amount of CFC-11 released from Sample-B1 ranged from 80 to 92 mg CFC-11/g PUR.

Table IV. 6 CFC-11 released from the polyurethane sample incubated at 100°C for 24 hours

Sample	**mg CFC-11 /g PUR**
B1-1-24-100	90.07 ± 1.85
B1-2-24-100	81.26 ± 1.93

Same samples were incubated for 24 more hours at 150°C and 180°C to determine the effect of temperature on the release of CFC-11. However, it was observed that the structure of foam samples was deformed at 150 °C and 180 °C (Figure IV. 4). Besides, the amount of CFC-11 determined in these experiments was much lower than the results obtained at 100°C. The reason of lower amounts of CFC-11 determined in samples incubated at 150 °C and 180 °C could be the combustion of CFC-11 at high temperatures. Therefore, the optimum temperature to enhance the release of CFC-11 within PU foam was chosen as 140°C.

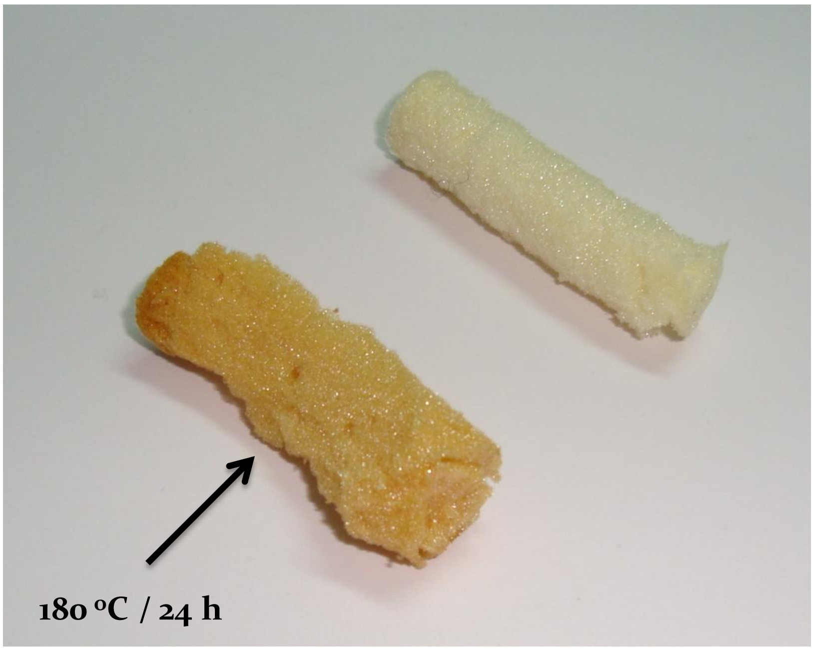

Figure IV. 4 Effect of heat on PUR foam

IV.2.2 Incorrect Results Due to Sealing the Bottles with Used Septa

Samples were placed in bottles following the removal of 1-cm diameter samples from the panel. They were then sealed with PTFE-lined silicon septa and screw caps with aperture to enable withdrawal of CFC-11 samples with a syringe from the bottle. Three samples were taken from right side of the refrigerator unit and incubated at 140°C for 48 hours. Since all new septa were exhausted, samples C1-2 and C1-3 were placed in bottles where were sealed with septa used in earlier experiments. Only sample C1-1 was placed in a bottle capped with an unused septa. Results show that CFC-11 release from C1-1 was 113-118 mg CFC-11/g PUR (Table IV. 7). Less amounts of CFC-11 was released from C1-2 and C1-3 in comparison to C1-1. These results showed that CFC-11 escaped through the needle holes on the re-used septa which were created while taking gas samples with the syringe. The temperature increasing from room temperature (20°C) to 140°C caused overpressure and resulted in more CFC-11 leak. As depicted in the equation below, the pressure in the bottle incubated at 140 °C is calculated as 1.93 atm.

$$\frac{P_1}{P_2} = \frac{T_1}{T_2} \qquad \frac{1\ \text{atm}}{P_2} = \frac{293\ \text{K}}{413\ \text{K}}$$

At the end of the incubation period, it was observed that septa bended slightly outwards as a result of over-pressure.

Table IV. 7 CFC-11 amount remaining in the right-side panel of refrigerator

Sample	mg CFC-11 /g PUR
C1-1-48-140	115.2 ± 2.60
C1-2-48-140	108.1 ± 1.16
C1-3-48-140	84.35 ± 2.30

Less CFC-11 was determined in C1-3, because after gas sampling it was noticed that the bottle in which C1-3 was placed has been sealed with a septa with more holes than the septa used for the bottle of C1-2.

IV.2.3 Amount of CFC-11 Determined in Foam Samples

Core foam samples cut out from the panels A1 and A2 from the bottom of the refrigerator unit was analyzed for CFC-11 (Figure IV. 5). Results are given in Table.

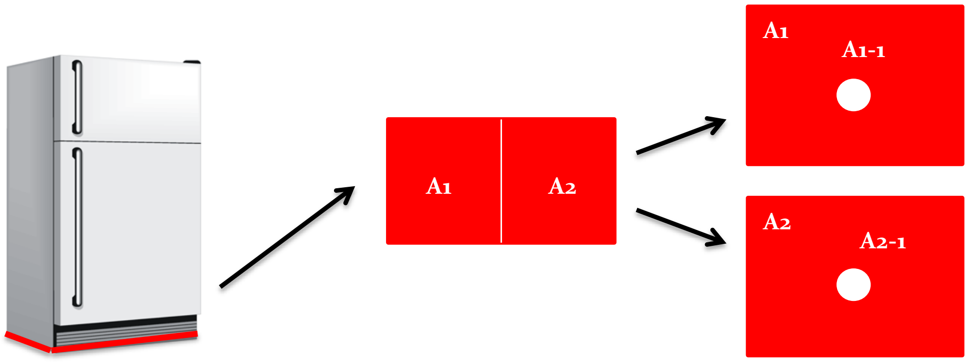

Figure IV. 5 Sampling from bottom side of the refrigerator

Table IV. 8 CFC-11 amount released from the bottom panel of refrigerator (140°C / 48 h)

Sample	mg CFC-11 /g PUR
A1-1-48-140	141.86 ± 1.65
A2-1-48-140	136.00 ± 2.97

Results obtained from both panels (A1-1 and A2-1) were similar. It is concluded that the average CFC-11 content in the bottom part of refrigerator was between 135-142 mg CFC-11/g PUR. In one study, the average blowing agent

(CFC-11) content released after first heating step (at 140°C for 48 hours) was reported as 12.7 ± 2.90 % w/w or 98-156 mg CFC-11/g PUR [40]. Results of this study showed were comparable to the results obtained from this study; minor differences may have resulted from the minor differences in manufacturing.

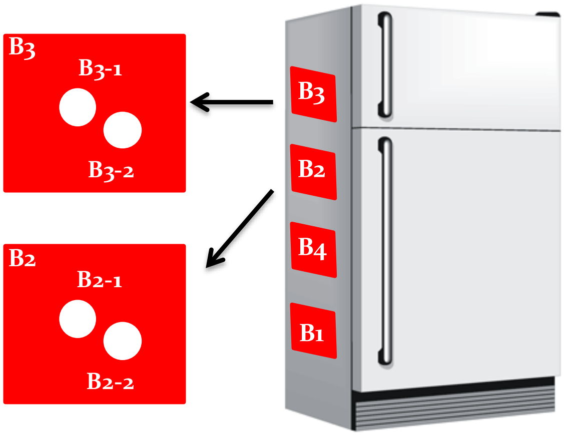

Figure IV. 6 Sampling from left-side freezer-part of the refrigerator

Core foam samples cut out from the panels B2 and B3 from the left-side freezer-part of the refrigerator unit was analyzed for CFC-11 (Figure IV. 6). Results are given in Table IV. 9. CFC-11 remaining in Sample-B2 was 179-194 mg CFC-11/g PUR, while Sample-B3 contained 172-187 mg CFC-11/g PUR. Average CFC-11 content contained in top panel was 176.19 ± 1.71 mg CFC-11/g PUR.

Table IV. 9 CFC-11 amount released from the left freezer-panel of refrigerator (140°C/48 h)

Sample	**mg CFC-11 /g PUR**
B2-1-48-140	193.7 ± 1.40
B2-2-48-140	179.9 ± 1.98
B3-1-48-140	172.5 ± 1.60
B3-2-48-140	186.4 ± 1.94

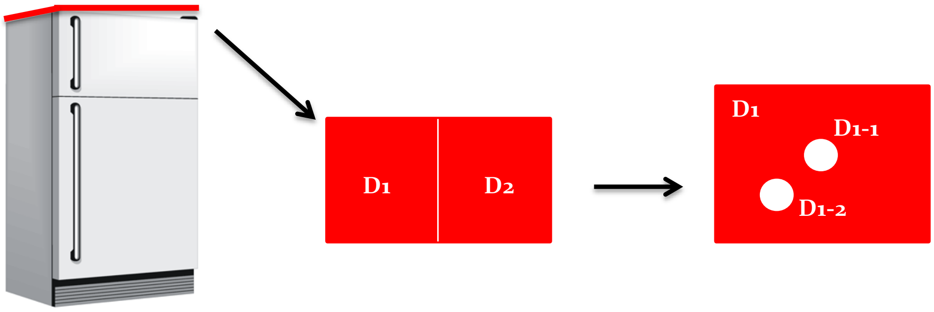

Figure IV. 7 Sampling from top side of the refrigerator

Finally, Core foam samples cut out from the panel D1 from the top side of the refrigerator unit was analyzed for CFC-11 (Figure IV. 7). Results are given in Table IV. 10. Average CFC-11 content of the panel was 176.2 ± 1.2 mg CFC-11/g PUR.

Table IV. 10 CFC-11 released from the top panel of refrigerator (140^{o}C / 48 h)

Sample	mg CFC-11 /g PUR
D1-1-48-140	175.3 ± 0.79
D1-2-48-140	177.1 ± 1.97

Results from each experiment are summarized in Table IV. 11. Values ranged from 79 mg CFC-11/g PUR to 191.36 mg CFC-11/g PUR. The lowest values were obtained from left (fridge) side. However, these samples were incubated only 24 hours at 100^{o}C. Thus, the results are not considered representative of the actual CFC-11 values contained within the foam, because samples from right, refrigerator door and bottom panels (incubated at 140^{o}C for 48 h) gave compatible and higher results. Highest values were obtained from left (freezer) and top side of the refrigerator. During sampling, it was observed that foam panels taken from the freezer were thicker (Figure IV. 8). Foam sample from freezer-part had a length of 6 cm, while foam taken from fridge-part was only 4 cm long.

Figure IV. 8 Foam samples from freezer and fridge

In the study of Scheutz et al., 2007, total BA content in the insulation foam was 116-182 mg CFC-11/g PUR [40]. Total BA content was calculated as the sum of CFC-11 release from two heating steps and release during sampling of the foam. On the other hand, first heating step resulted in a release of 98-156 mg CFC-11/g PUR. In this study, only one heating step is applied, and the results were demonstrated in Table IV. 11.

Table IV. 11 Average CFC-11 content remaining in the end-of-life refrigerator

Sample	mg CFC-11 /g PUR
Right	115.2 ± 2.60
Left (Freezer)	183.11 ± 8.25
Left (Refrigerator)	86.29 ± 5.0*
Top	176.19 ± 1.71
Bottom	138.9 ± 3.84
Fridge door	147.5 ± 1.62

* incubated at 100^{o}C / 24 h

Minimum amount of CFC-11 remaining in foam was 113 mg CFC-11/g PUR and the maximum was 191 mg CFC-11/g PUR.

Polyurethane foam contained within the refrigerator may vary in weight and accordingly the amount of CFC-11. The amount of CFC-11 that will be released from 2.24 million refrigerators is calculated again with the results obtained from this study. Total amount of CFC-11 release will be between 1011 and 1708 ton.

IV.2.4 Determination of CFC-11 Loss during Sampling

In order to determine the amount of CFC-11 released during sampling, a 500-ml (exact capacity: 630-mL) glass bottle was also put in the glove bag and capped before the glove bag is opened after sampling. Results are given in Table IV. 12 below.

Table IV. 12 CFC-11 loss during sampling

Sample	**mg CFC-11 /g PUR**
Right	10.77 ± 0.89
Fridge door	9.37 ± 0.10
Left (Freezer)	9.97 ± 0.18

A study informed that the sampling may release from 3 to 35 mg CFC-11/g PUR [40]. Sampling loss in this study was determined to vary between 9.27 and 11.66 mg CFC-11/g PUR. The average BA (CFC-11) release is summarized in Table IV. 13.

Table IV. 13 Total average CFC-11 content in the refrigerator

	mg CFC-11 /g PUR
Sampling loss	10.04 ± 0.70
Heating step	162.5 ± 24.7

CHAPTER V

CONCLUDING REMARKS & RECOMMENDATION

In scope of this study, number of refrigerators containing rigid polyurethane foam and total amount of CFC-11 in PU foam were investigated. The major conclusions obtained from this study and the recommendations for future researches are summarized below:

Refrigerators sold between 1986 and 1995, containing PUR foam blown with CFC-11, were determined as 7 million. With the help of a model obtained from existing literature, number of refrigerators that are still in use is determined as 2.24 million. PUR foam within these refrigerators is 8944 tons considering that a refrigerator includes 4 kg of PUR on average. Literature survey, on the other hand, indicated that up to 90% of initial CFC-11 amount would remain in end-of-life refrigerators. Taking this into account, total amount of CFC-11 in PU foam of 2.24 million refrigerators is calculated as 1037 tons.

In a similar effort to estimate the total amount of CFC-11 trapped in PU foams in end-of-life refrigerators; a refrigerator produced in 1993 and no longer in use, was disassembled and the foam inside was analyzed for its CFC-11 content. Foam samples were incubated at 140^{o}C to release CFC-11 contained in the foam and CFC-11 analyses were done on gas chromatography-mass spectroscopy. The results revealed that the heating step applied to the samples prior to CFC-11 analysis by GC-MS drove out 113 to 191 mg CFC-11/g PUR, while loss from cutting of foam samples was between 9.3 and 11.7 mg CFC-11/g PUR. Based on the analysis results obtained from the experimental phase of the study, total amount of CFC-11 in PU foams in end-of-life refrigerators is recalculated. It was concluded that these refrigerators will release between 1011 and 1078 tons of CFC-11. When the total amount of CFC-11 predicted based on the analysis results (1011-1708 tons) and based on the literature survey (1037 tons), it can be concluded that both approaches result in similar predictions. However, it is important to note that CFC-11 analysis method established in this study can be used to ascertain CFC-11 amounts in refrigerators produced by different manufacturers to designate average amount of CFC-11 in refrigerators. Nevertheless, results from this study and literature survey showed that the amount is expected to be 1000-2000 tons. Moreover, a survey can be conducted in Turkey to evaluate the number of pre-1996 refrigerators in use.

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