IZMIR KATIP CELEBI UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

SYNTHESIS OF IMIDAZOLE DERIVATIVES AND THEIR BINDERLESS IMMOBILIZATION TO FABRIC TO LOAD ANTIBACTERIAL PROPERTIES

M.Sc. THESIS

Nurgül MUTLU

Department of Materials Science and Engineering

Thesis Advisor: Assoc.Prof. Dr. Şerafettin DEMİÇ

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İZMİR KÂTİP ÇELEBİ ÜNİVERSİTESİ FEN BİLİMLERİ ENSTİTÜSÜ

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YÜKSEK LİSANS TEZİ

Nurgül MUTLU

(Y130111037)

Malzeme Bilimi ve Mühendisliği Anabilim Dalı

Tez Danışmanı: Doç. Dr. Şerafettin DEMİÇ

MART 2017

Nurgül MUTLU, a M.Sc. student of IKCU Graduate School of Science Engineering and Technology student ID Y130111037, successfully defended the thesis entitled **"SYNTHESIS IMIDAZOLE DERIVATIVES AND THEIR BINDERLESS IMMOBILIZATION TO FABRIC TO LOAD ANTIBACTERIAL PROPERTIES"**, which she prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

Thesis Advisor : **Assoc. Prof. Dr. Şerafettin DEMİÇ** .....
Izmir Katip Celebi University

Jury Members : **Asst. Prof. Dr. Fethullah GÜNEŞ** .....
Izmir Katip Celebi University

Asst. Prof. Dr. Candan AKCA .....
Izmir Katip Celebi University

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To my family,

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ABBREVIATIONS

DMSO : Dimethyl Sulfoxide

HCl : Hydrochloric Acid

KOH : Potassium Hydroxide

HNO_3 : Nitric Acid

H_2O_2 : Hyrdogen Peroxide

H_2O : Dihydrogen Monoxide

O_2 : Oxigen

^{13}C-NMR : Carbon Nuclear Magnetic Resonance

^{1}H-NMR : Proton Nuclear Magnetic Resonance

WI : Whitness Index

YI : Yellowness Index

ICP-MS : Inductively Couples Plasma Mass Spectrometer

SEM-EDX : Scanning Electron Microscopy with Energy Dispersive X-ray

FT-IR : Fourier Transform Infrared

Ppm : Parts per Million

MIC : Mimimum Inhibitory Concentration

MHz : Megahertz

SYMBOLS

C* : Concentration

h : Hour

b* : Yellow-Blue Axis

t : Time

L* : Color Span

α* : Green-Red Axis

h* : Color Type

C : Celsius

H_2O : Dihydrogen Monoxide

O_2 : Oxigen

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SYNTHESIS IMIDAZOLE DERIVATIVES AND THEIR BINDERLESS IMMOBILIZATION TO FABRIC TO LOAD ANTIBACTERIAL PROPERTIES

SUMMARY

The compounds bonded with functional groups in textile materials carry the economical support material property. The complex and/or organic compounds with the desired properties can be immobilized into the textile materials by using the reactivity of hydroxyl groups of cellulose and the NH2 groups in wool. Most of commercially purchased silver salts show a rapid release of silver in water because of their ionic structure. For this reason, they exhibit high antibacterial activity but the short-term. N-heterocyclic carbene (NHC) complexes have the long-term antibacterial effects by releasing the silver ion into solution gradually. Recently, the studies on the reactions about catalytic activities of silver NHC compounds have also increased. It is aimed to synthesize the light resistant, antibacterial and catalytic effective complex and also to immobilize this complex into the fabric by considering the light sensitivity of silver compounds. In the light of this information, synthesis, physical properties, and antimicrobial activities of imidazole based 1,3-disubstitue imidazolium silver (I) complexes have been targeted.

The structure of synthesized compounds was determined by FTIR, NMR. The light stability of the complexes and antibacterial effectivities was investigated, then the complexes which are stable to light and exhibit antibacterial effectivity was immobilized to wool fibers with functional groups of the complexes. The immibolization was created with chemical bonding between the wool fabric and the synthesized compounds. The metal content of the immobilized complexes was analyzed by ICP and their surface characterization was identified by SEM. After the measurements of antibacterial effectivity and washing durability of immobilized complexes, color changing which is a general problem of silver compounds was measured using spectrophotometer. The antibacterial effectivities of the modified fibers were investigated by quantitative method at pre-washing and after sequence washings.

İMİDAZOL TÜREVLERİ İÇEREN BİLEŞİKLERİN SENTEZİ, KUMAŞA BİNDERSİZ İMMOBİLİZASYONU İLE KUMAŞA ANTİBAKTERİYEL ÖZELLİK KAZANDIRMA

ÖZET

Tekstil materyalleri yapılarındaki fonksiyonel gruplarla bağ yapacak bileşikler kullanıldığında ekonomik bir destek maddesi özeliği taşırlar. Selülozda hidroksil grupları, yünde NH2 gruplarının tepkinliği kullanılarak istenen özeliği taşıyan kompleks ve/veya organik bileşiklerin tekstil materyaline immobilizasyonu sağlanabilmektedir. Gümüş kimyasında ticari olarak satın alınan gümüş tuzlarının çoğu iyonik yapıda olduğu için sulu ortamda hızlı Ag salınımı gösterirler bu da onların yüksek ancak kısa süreli antibakteriyel etkinlik sergilemelerine neden olur. N-heterosilik karben (NHC) kompleksleri ise gümüş iyonunu çözeltiye yavaş yavaş bırakabilme özeliklerinden dolayı uzun süreli antibakteriyel etki gösterebilmektedirler.Gümüş bileşiklerinin ışığa karşı hassasiyeti de göz önüne alınarak ışık dayanımı olan, antibakteriyel ve katalitik özelik sergileyebilecek komplekslerin sentezlenmesi ve kumaşa immobilizasyonu hedeflenmektedir. Bu bilgiler ışığında imidazol temelli 1,3-disübstitue-imidazolyum gümüş (I) komplekslerinin sentezi, fiziksel ve antibakteriyel özelliklerinin incelenmesi planlanmaktadır.

Sentezlenen bileşiklerin yapıları, FTIR, NMR ile aydınlatıldı, komplekslerin ışığa karşı dayanımları ve antibakteriyel etkileri incelenerek, ışık dayanımı olan ve antibakteriyel etki gösteren kompleksler içerdikleri fonksiyonel grub ile yün kumaşa immobilize edildi. Bu immobilizasyon yün kumaş ve sentezlenen bileşik arasında kimyasal bağ kurularak oluşturuldu. İmmobilize edilmiş kumaş numunelerinin içerdiği metal içeriği ve tutundurma sonrası analizi ICP ve SEM ile karakterize edildi. Modifiye kumaşların antibakteriyel etkinliği, yıkama dayanımı ve spektralfotometre cihazı ile gümüş bileşiklerinde sıkça rastlanan kumaştaki renk değişimi (kararma) testleri yapıldı. Kumaşların antibakteriyel etkinliği yıkama öncesi ve ardışık yıkamalar sonrası kantitatif yöntemle araştırıldı.

1. INTRODUCTION

1.1 The Textile Sector in the World and Turkey

With the growing demand for textile products, global textile industry has increased rapidly in recent years. This sector has historically been highly protected and inward oriented. Industrialization generally increased with the textile sector [1]. The Textile Agreement was signed by the World Trade Organization (WTO) in 1995 and China is a member of the WTO in 2001, it ushered in a new era in world textile sector. In 2000, the US and EU became the largest importers in textiles, while China became the largest exporter. Thus, World textile exports increased by 17% in 2011. Because of the Textile sector plays an important role in the development of our country with the added-value and export share [2].

Turkey's share in the EU's apparel market was 11.7% in 2015. Additionally, Turkey's share, in the first six months of 2016, increased 5.7% and became 12.7% as compared to the same period of 2015. Turkey ranks third in the market share following China and Bangladesh that the EU countries imported apparel products [3]. As shown in Table 1.1 according to market share indicator that Turkey is growing day by day in this sector. EU countries have maintained their largest buyer position with having their productions made from major producer countries such as China, Turkey, Bangladesh and India [2].

Table 1.1 : Turkish Market Share [2].

MARKET SHARE%		2014 ANNUAL		2015 ANNUAL		CHANGE %		2015 JANUARY-JUNE		2016 JANUARY-JUNE		CHANGE %	
	EU_EXTRA	100 KG	EURO	100 KG	EURO	100 KG	EURO	100 KG	EURO	100 KG	EURO	100 KG	EURO
1	CHINA	42,2	38,8	39,6	37,6	-6,2	-3,3	36,9	34,5	35,1	31,5	-4,9	-8,8
2	BANGLADESH	15,5	13,9	16,8	15,5	7,8	11,7	17,8	16,6	18,6	17,6	4,3	5,6
3	**TURKEY**	**9,3**	**12,6**	**9,4**	**11,7**	**1,3**	**-7,2**	**9,4**	**12,0**	**9,7**	**12,7**	**3,1**	**5,7**
4	INDIA	7,7	6,9	8,2	6,9	5,8	-0,2	9,0	8,0	9,1	7,9	1,4	-1,5
5	PAKISTAN	6,3	3,8	7,0	4,1	10,4	9,5	7,2	4,3	7,7	4,6	6,7	5,6
6	VIETNAM	2,7	2,9	2,8	3,3	4,3	13,3	2,6	3,1	2,7	3,4	4,1	10,1
7	CAMBODIA	2,3	2,7	2,7	3,3	17,1	19,6	2,4	3,0	2,7	3,5	12,7	18,2
8	MOROCCO	1,7	3,0	1,8	2,7	7,8	-7,6	2,0	3,0	1,9	3,3	-3,2	9,5
9	TUNISIA	1,6	2,7	1,6	2,4	-0,4	-12,1	1,7	2,7	1,6	2,6	-5,3	-2,7
10	SRI LANKA	1,3	1,8	1,3	1,8	1,1	-1,5	1,4	1,9	1,5	1,8	8,5	-6,6

The day-to-day development of the textile industry depends on the protection of supply and demand equilibrium. This balance is only possible to keeping up with the developments.

The product range in the textile sector is constantly expanding [4]. Developments in the past century have changed people's understanding of quality. The change of sense of quality, sensivity, comfort and cleanliness have become more important for consumers. So, this led to the differentiation of traditional textile products.

Textile products depend on parameters such as traditional model, color, material differentiation. New products are added every day to the products presented to the consumers depending on the innovations in the functional features. Textile products which are traditionally used for covering, protection, ornamenting are produced in new features that will fulfill these needs in addition to other functions. Product properties of different sectors such as health, security, information, cosmetics are being imparted to flexible textile products with barrier properties and textile products that can perform new and different functions without deterioration in image and usage comfort features are being developed [4]. Textiles for domestic use as well as for industrial use developed for the specific purpose other than conventional textile known in recent years as research result are on the agenda [2].

1.2 The Importance of Microorganisms and Their Impact on Textile Products

Microorganisms are very small organisms that they can not be seen with the eye, but they can be seen with the microscope[4]. Micro organisms are cellular structured organisms which have a polysaccharide-containing outer wall, a layer of membrane just beneath, and innermost organelles with enzymes and nucleic acids. [5]. The microorganism term generally includes bacteria, fungi (molds and yeasts) and viruses [6]. There are many different types of microorganisms in different characteristics that can survive in many different environments, from ice to superheated water [4]. Microorganisms are in the air, in our bodies, in the soil, and on all the surfaces[7,8]. Microorganisms lives harmony with in different part of human body [4]. Nutrient resources, adequate temperature and moisture are suitable conditions for growth of bacteria. Many parts of the human body have microscopic organisms. Our skin is surrounded by countless small organisms and most of them are natural protection

layer and skin flora. Opportunistic infections and organisms that are considered as members of the normal flora are a frequent problem. Bacteria are the most common members of the normal flora, especially it observed in mucosa and some of them are anaerobic form [9-13].

Textile materials is suitable environment of these organisms to survive on human skin [4]. Especially bacteria and fungi are important in textile products. Microorganisms begin to develop in the presence of some moisture and proper food, and under ideal conditions, microbial growth develops very rapidly and maintains its presence even under severe conditions. When you start with a single bacterium, after about 9 hours, 6 billion bacterias occur and its equal to the number of people on earth [14,15].

In general, bacterias cause malodor; Fungi cause biodegradation and spotting. Many bacteria grow at 30-37 $^{\circ}$C optimal temperature while fungi need 25-30 $^{\circ}$C optimal range [16]. Bacteria are examined in two parts: pathogenic and non-pathogenic. Table 1.2 shows some pathogenic and non-pathogenic microorganisms [17].

Table 1.2 : Some Pathogenic and Non-Pathogenic Microorganisms [17].

Microorganism	Pathogenicity	Effects
Bacillus Subtilis	In general, its not pathogen	Spoilage of food, conjunctivitis
Eschericha Coli	Low pathogen	Spoilage of food, urinary infection
Klebsiella Pneumoniae	Pathogen	Pathogen Pneumonia, urinary tract infection
Pseudomonas Aeuroginosa	Low pathogen	Various infections
Protcus Vulgaris	Low pathogen	Inflammation
Staphylococcus Epidermidis	Low pathogen	Surgical wound infections
Staphylococcus Aureus	Pathogen	Toxic shock, purulence, abscess, fibrin clotting, endocarditis

It is necessary to get under control microorganisms because they cause malodour and appearance in the textine products. Because it is significant to prevent multiplication of pathogenic microorganisms due to the hazardous effects on human health [18]. Local temperature changes in the body activity are a trigger for the increase of these bacteria [4]. Sweat formation in the body provides ideal conditions for bacterial and fungal growth and development. There are 2-3 million sweat glands in the human body, distributed over the whole body surface [19]. These micro-organisms, which are examined by the microbiology scientist, cause negative effects such as loss of

performance, color change, malodour in textile products [4]. Since textiles provide the environment for growth of microorganisms, as well as stronger growth of microorganisms leads to bad smells (fabric, socks, etc.), visual distortions and color changes (such as curtains, carpets, different home furnishings, etc.), reducing the life expectancy of products (Especially cotton and wool-containing products) it can also cause potential hazards to human health. This, in some cases, may mean that a hygienic and aesthetic material can not be used [9]. The presence of nutrient sources (various food impurities, oil, protein, sugar and leather residues) on textile products is emerging as a major factor accelerating microbial breeding on textile materials.

This can cause the textile product to become unusable from hygienic and aesthetic care. Such microbiological developments on textile surfaces are also a potential health threat. The regional temperature changes in the body during active activity are a trigger for the multiplication of these bacteria [4].

Microorganisms cause the following damages in textiles, clothing and footwear:

1. Loss of strength of the fabric due to fiber deterioration (mold); synthetic fabrics and tent fabrics, nets, tarpaulins, yarns.

2. Odor formation and staining marks; in socks, underwear and shower curtains.

3. Hygienic problems; pathogenic infections in textile used in hospitals [4].

As a result of adhesion of microorganisms on the surfaces of fabrics (adhesion), textile materials can be carriers. Therefore, garments such as medical supplies, surgical dressers, hospital curtains, nurse clothes, floor coverings and bedding materials, towels and worker uniforms must acquire antimicrobial function [20-21].

1.3 Antimicrobial Substance

Antimicrobial substance is an agent that kills microorganisms e.g bacteria, mold, yeast and fungus or inhibits their growth. Bactericidal, bacteriostatic, fungicidal, funguistatic or biocidal are just a few examples of commonly used terms of define the nature of antimicrobial activitiy. The Figure 1.1 is used to clarify and distinguish between these. If an active principle has a unfavorable effect on the vitalty of microorganisms, this is usually referd to as antimicrobial activity. If the active principle affects only bacteria or fungi, this is refferd to as antibacterial or

antimycotic activity respectively. The degree of the effect is denoted by –cidal (lethal) where there is significant germicidal activity, or -static where the active substance serves to inhibit the growth of bacteria [23].

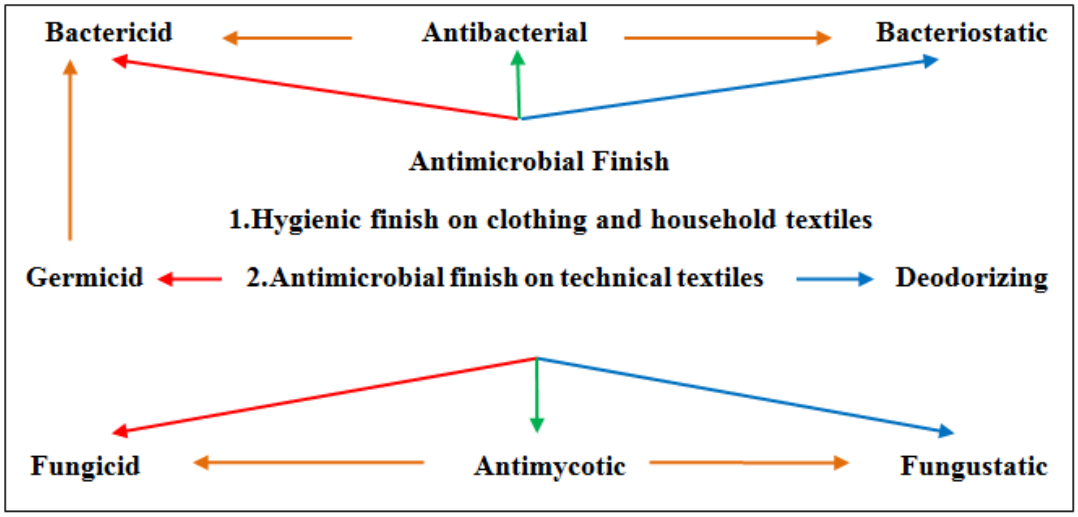


Figure 1.1 : Differentiation of Antimicrobial Activity [23].

Antimicrobials substances can be disunited into two categories based on the abilities against microorganisms:

1. Biocidal fucntions: Inactivation of microorganisms on the materials of total kill.

2. Biostatic functions: Inhabiyion of the growth of microorganisms on the materials or partial kill [23].

In addition, bacteriostatic and bactericidal activity is shown in Figure 1.2 [4].

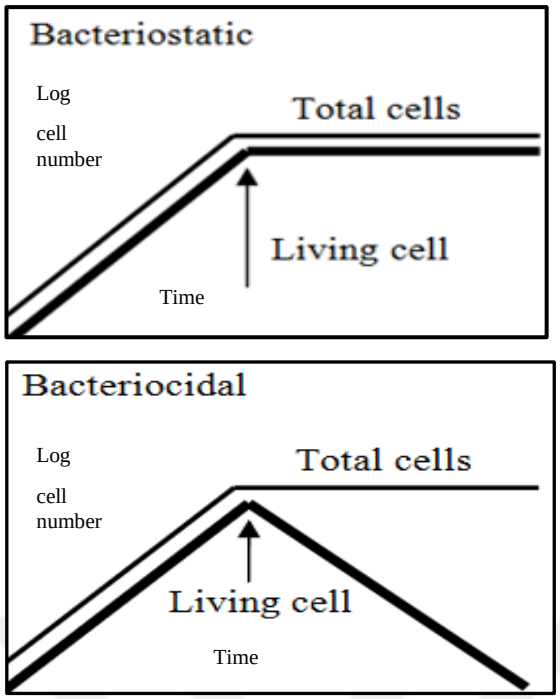


Figure 1.2 : Bacteriostatic and bacteriocidal activity [4].

The most common agents used in antimicrobial applications are triclosan, quaternary ammonium salts and metals (silver, copper, zinc, etc.). Other than these, studies on the use of many active substances such as halamine derivatives, chitosan are also being carried out [24]. Table 1.3 shows some antibacterial substances [25].

Table 1.3 : Antibacterial Agent [25].

Organic Compounds	**Halogenated Diphenyl Ethers (e.g., Triclosan)** **Phenol Compounds** **Halopenoics and Bisphenolic Compounds** **Resorcinol and derivatives** **Benzoic Esters** **Quaternary Ammonium Compounds**
Metals	Silver Zinc Copper
Other Inorganic Compounds	Zeolites NaAl-Silicate

In order to achieve the desired antibacterial effect, antibacterial materials may be used individually or in combination depending on the requirements and application.

1.4 Effect of Antimicrobial Substances on Textile Products

There are thousands of chemicals on Earth that kill microorganisms. However, most of them can be toxic for humans and the environment in practice. Therefore, an antimicrobial substance to be used in the textile industry should not only kill microorganisms, but also be safe for human and environment, and should not affect other properties of textile material in the negative direction [6,10]. When considering

past years antibacterial applications have been especially aimed at protecting the product.

The use of antimicrobials substances on textiles is based on very ancient time. For example, Ancient Egyptians used spices and herbs to preserve mummy wraps. In 1935, German scientist Domagk, was developed antimicrobial substances and this substances were based on quaternary ammonium salts. These was a significant parts of antimicrobial agents [26]. Altough people have used natural materials to combat diseases for millenia, and we have known that bacteria and microbs cause diseases for centuries, only in the twentieth centruy we begin to produce antimicrobial composition and add them to textile materials. During World War II, cotton fabrics were used extensively for tentage, tarpaulins and truck covers, for the protection of fabrics from rotting. This was a problem, especially in the southern pacific forest area. During the early 1940, the U.S army quartermaster corps collected and compiled data on fungi, yeast and algae isolated from textile in tropical and subtropical areas throughout the world. Military fabrics were treated with various materials. For example, after the world war and in the 1950's, fungicides were used in cotton fabrics [23].

It is known that ancient Chinese have similar applications. The archaeological discoveries made in Shanghai in the 1970s, the capital of China, made it clear that silk-made textile materials have been very well preserved for thousands of years [27]. It has only been in recent years to develop antimicrobial chemicals or fibers that can be applied to all kinds of textile products, especially clothes, and which can exactly fulfill the above expectations, even though the applications in this respect are very old. The antimicrobial materials used in the textile industry are generally developed by adapting the active ingredients widely used in food, cosmetics and medicine for many years to textile applications [8].

Many antimicrobial materials have been developed that can be used in the textile industry. These materials vary greatly according to the chemical structures, the working mechanisms, the effects on humans and the environment, on the properties of the products they adhere to, on their resistance to various external influences, their prices and their interactions with microorganisms [25].

Textile products that are given antimicrobial properties help to reduce and eliminate the negativity caused by micro organisms. Therefore, antibacterial dressing in clothing is increasingly important day by day.

1.5 Advantages of Using Antimicrobial Substance on Textile Products

The conventional fibers and polymers resist the growth of microorganisms and their accumulation in the environment. Textiles are a convenient environment for the rapid growth of microorganisms.Temperature, humidity, dust, soil,skin dead cells, sweat, spilled food and drink stains accelerate the creation of medium [28,29]. With the rapid development of the hygienic standard of living, it has focused on the antibacterial modification of textiles [30].

Uncontrolled proliferation of microorganisms causes color and odor disorders in textile material and affects the mechanical strength property negatively. It also leads to the spreading and spreading of microorganisms and the spread of infections [31]. Because of this, antibacterial textile products are gaining importance everyday. Besides the immediate improvement of human life, the control of the harmful infulances of microorganisms is also necessary. A wide variety of microorganisms coexists in a natural balance with the human body and living environments, but they can cause some critical problems by producing rapid and uncontrolled rapid microbes [32].

Antimicrobial substances are use to prevent three undesirable effects in textiles [33].

1. The first includes the degradation phenomena like coloring, staining and deterioration of fibers [34].

2. Malodor produces [35].

3. The increase of potential health risks [36].

Moreover, it is very important for the antibacterial properties that it is very simple to apply and it is suitable for any kind of system, does not require additional production process and does not release volatile organic compound. In addition, it is effective throughout the use of the product and is more advantageous than disposable products.

1.6 Antibacterial Fibers and Antibacterial Fabrics

Table 1.4 shows the types of antibacterial fiber and antibacterial fabric.

Table 1.4 : Antibacterial Fibers and Antibacterial Fabric Constructions**.**

Antibacterial Fibers		Antibacterial Fabric Constructions
Natural Fibers	Synthetic Fibers	Weaving
Bamboo Fibers	Polyester	Knitting
Aleo vera Fibers	Polyamide	Non woven
Cotton	Polypropylene	
Silk	Polytetrafluoroethylene	
	Carbon	
	GlassFiber	

1.6.1 Antimicrobial Properties of Fibers

They are fibers that have antimicrobial properties due to their chemical structure. These fibers are thought to neutralize microorganisms by their antimicrobial or surface properties. For example; chitosan, chitin bamboo fibers.

1.6.2 Antimicrobial Fiber Production

It is carried out by the participation of antimicrobial substances in the fiber structure. This can be done during the polymerisation phase or during the fiber shooting phase of the fiber production.

1.7 Imparting Antimicrobial Properties to Textile Materials It is possible to impart antimicrobial properties to textile materials in three ways.

1. Use of antimicrobial fibers in the production of textile materials.

2. Imparting antimicrobial properties during fiber shooting on fibers used in the production of textile materials.

3. Imparting antimicrobial properties to textile materials during finishing processes.

1.7.1 Imparting Antimicrobial Properties to Fibers During Polymerization

The use of organic or inorganic antimicrobials for the production of polymers which are shooted to fibers during the polymerisation process is not widely used because it is an expensive method.

1.7.2 Imparting Antimicrobial Properties to Fibers During Fiber Shooting

The most commonly used method for synthetic fibers is the addition of antimicrobials during fiber shooting. This method;

1. Fiber shooting from melt.

2. It is also used in the electro-shooting method.

The antimicrobial activity of the fibers produced by this method is more permanent, and the washing and abrasion resistance is higher. Antimicrobial materials must have some properties in order to be used in the fiber shooting processes.

1.Does not react with the polymer used in the fiber shooting.

2.The properties of the produced fibers should not be adversely affected.

3.Must be resistant to high temperatures .

4. Does not affect the dyeing and finishing operations applied to the fibers.

5.It should not be affected by finishing and dyeing operations applied to the fibers.

1.7.3 Imparting Antimicrobial Properties to Fibers During Shooting From Melt

The antimicrobial and polymer particles are fed together at a suitable mixing speed and heated extruder .Then, the polymer and antimicrobials are mixed for a specific period of time. This mixing process provides homogeneous dispersion of the antimicrobial materials in the polymer and is very important in terms of the properties of the final product produced.

There are many studies about imparting antimicrobial properties to fibers during fiber shooting. Kalyon and Olgun found that the composites they produced by mixing triclosan with polymers according to the fiber shooting method showed antimicrobial activity against Gram positive and Gram negative bacteria in their study [91]. Conventional antimicrobials can be used in the melt shooting method, as well as in metal and metal oxide powders due to its high temperature and chemical resistance in fiber shooting processes. Damm et al. produced polyamide 6 composites containing silver nanoparticles and microparticles using the fiber shooting method from the melt [92]. They compared the antimicrobial activities of nano- and microcomposites they produced and determined that nanocomposites were more effective. Damerchely et al. also used nylon-6 and silver nanotubes at different ratios in the extruder using fiber shooting method and produced nanocomposite multifilaments. They found that the filaments they obtained were effective against Gram positive and Gram negative bacteria.

1.7.4 Imparting Antimicrobial Properties to Fibers During Electroshooting

Another method used in the field of antimicrobial fiber is electrospinning. In this method, fiber-drawing solutions are prepared by mixing the polymers dissolved in the appropriate solvent or melting at the appropriate temperature with antimicrobial materials, and the prepared solution solutions are passed through the micrometer small scale, and are directed in the electric field and deposited on the collecting surface in the form of nanofibers. Recently, many studies have been carried out on the production of antimicrobial nanofibers. Tan and Obendorf produced polyamide-6 membranes using three different N-halamins in their work and tested their properties and antimicrobial activity. As a result of the tests, it was found that the membranes produced showed antimicrobial activity against Gram positive and Gram negative bacteria even at short contact times. It has also been determined that the N-halams incorporated into the structure do not affect the mechanical properties of the membranes, but that the matrix of the polyamide-6 changes the crystal structure. Son et al. found that the cellulose acetate / Ag nanofibers obtained by dissolving $AgNO_3$ and cellulose acetate in diluted acetone have a strong antimicrobial activity against both Gram negative and Gram positive bacteria. Nano-sized antimicrobial materials can be easily used in the electro shooting method. For example, Duan et al. have produced nanofibers using poly (-caprolactone) and silver-loaded zirconium

phosphate nanoparticles and have proven their antimicrobial activity [75]. Likewise, Lee et al. produced antimicrobial polyurethane nanofibers containing ZnO nanoparticles [76].

1.7.5 Imparting Antimicrobial Properties with the surface coating method

It is generally applicable to all fiber types, but the wash strength of the applied antimicrobial finish is dependent on the affinity of the antimicrobial agent used. For this reason, they are applied together with polymeric coating products [37]. The work is done by Isquith et al. can be given as an example of a coating application. In this study, it has been revealed that coating of fabrics and other surfaces with products obtained from the hydrolysis of the trialkoxysilyl quaternary ammonium salt affords efficacy against a wide range of microorganisms and resistance to washing [38].

1.8 Antimicrobial Finishing Processes

Thanks to the antimicrobial finishing process it is possible to impart antimicrobial properties to fiber, yarn, fabric or all finished textile materials. During the antimicrobial finishing process, the antimicrobial materials dissolved in the finishing baths are transferred to the textile products using one of the dipping, fusing-drying, spraying or foam methods. It is also possible to impart antimicrobial properties to textile products by using the surface coating method.

The chemicals used in antimicrobial finishing processes must have certain properties.

1. Must be resistant to washing, dry cleaning and hot pressing operations.
2. Must have selective activity against unwanted microorganisms.
3. Must not have harmful effects on producers, users and the environment.
4. Must be suitable for chemical processes.
5. Implementation must be easy .
6. Must not affect fabric quality in the negative direction.
7. Must be resistant to body fluids.
8. Must be resistant to sterilization procedures.

Various methods have been developed for increasing the durability of the antimicrobial finishing process, such as using binder or crosslinking agents, encapsulating antimicrobial materials in fiber matrices, coating fiber, yarn or fabric surface, modifying the chemical structure of fibers to allow covalent bond formation. Antimicrobial finishing processes are divided into three basic groups.
1. Resistant to bio-degradation finishes.

2. Hygienic finishes.

3. Aesthetic finishes.

1.8.1 Resistant to Bio-degradation Finishes

This group contains finishes that prevent degradation of materials by providing long-term and short-term antimicrobial protection.

1.8.2 Hygienic Finishes

They are used to remove pathogenic (disease-causing) bacteria to control infection.

1.8.3 Aesthetic Finishes

It is the finishing material that protects textile materials from fading, staining and unwanted odors.

1.8.4 Chemical Bonding

Theoretically, it is the best way to achieve a robust ending process.This method gives good results in cellulose, wool and polyamide fibers. However, in order to obtain beter results, it is necessary to have suitable reactive groups on the fiber [37].

There are several ways to provide antimicrobial activity through chemical bonding. The application of the vaccine polymer, homopolymer and / or copolymers to the fibers is one of these ways. Vaccine polymers, homopolymers and copolymers; are commonly attached to fabrics to form a functional group that is positively or negatively charged on the fiber. Then, these fabrics are immersed in a counterbalanced solution. In one of the studies, vaccination polymerisation of cellulosic textiles containing poly(2-methyl-5-vinylpyridine) or polyvinylpyrrolidone and subsequent immersion of the aqueous potassium iodide provided the fabrics with resistance to Gram-positive bacteria and dermatophytic and mold fungi. This

technique brings iodophors, a slow releasing iodine material, to the fabric to impart antibacterial and fungicidal propertie [39].

Another method of chemical bond attachment is chemical fiber modification through the formation of covalent bonds. A good example of broad spectrum antimicrobial finishing process based on formation of covalent bonds with fibers is the reaction of poly(vinyl alcohol) and 5-nitrofurylakrolein [39]. A relatively new application, microencapsulation, is one of the ways in which antimicrobial activity is imparted to textiles via chemical bonds. Because antimicrobial containing capsules are covalently attached to the fibers. However, it is necessary to ensure that the capsule performs antimicrobial controlled release. If there is no release, the processed cotton fabric will not exhibit great antimicrobial activity. When the release is very fast, there is a problem with the wash strength.In addition, the capsules must be resistant to the processes commonly applied to fabrics and must be small enough to cause no change in the attitude and other properties of the fabrics. Cotton fabrics processed with this system exhibit great antimicrobial properties even after 100 washings [37].

1.9 Evaluation of Antimicrobial Efficacy

Test methods for the activity of antimicrobial testes are shown in table 1.5 [40]. These methods are categorized three groups. Antimicrobial methods have the agar diffusion method, suspension method and soil burial method [41]. The activities of the treated textiles are examined by these tests [42].

Table 1.5 : Antimicrobial Efficacy Tests [42].

SN 195920-1992 contains Textile fabrics, determination of the antibacterial activity and agar diffusion plate method.
SN 195921-1992 contains textile fabrics, determination of the antimycoticactivity and agar diffusion plate method.
AATCC 30-1993 Antifungal activity evaluation of textile materials, mildew and rot resistance in textile materials.
AATCC 147-1993 Antibacterial evaluation in textile fabrics paralel streak method.
AATCC 90-1982 Antibacterial efficiency on fabrics, detection of agar plate method.
AATCC 174-1993 Antimicrobial activity assessment of carpets.
JIS L 1902-1998 Testing method for antibacterial of textiles.
AATCC 100-1993 Antibacterial finishes on textile materials evaluation of textile materials parallel streak method.
SN 195924-1983 Textile fabrics: Determination of the antibacterial efficiency, germ count method.
XP G39-010-2000 Properties of textiles, textiles and polymeric surfaces having antibacterial properties. Characterization and measurement of antibacterial efficiency.
JIS Z 2911-1992 Methods for fungus resistance.
ISO 846-1997 Plastics and evaluation of the action of microorganisms.
ISO 11721-1-2001 Textiles and determination of resistance of cellulose containing
ASTM E2149-01 Standard Test Method for Determining the Antimicrobial Activity of Immobilized Antimicrobial Agents Under Dynamic Contact Conditions.
ISO 20743 "Textiles –Determination of the antibacterial activity of Antibacterial Finished products.

1.9.1 Agar Diffüsion Method

This type of test is illustrated AATCC 147-2004(American Association of Textile Chemists and Colorists), JISL 1902-2002 (Japanese Industrial Standards) and SN 195920-1992(Swiss Norm). This method is a preliminary test to determine the diffusive antimicrobial finish.It is not proper for textile materials and non diffusive finishes other than fabrics. They are only qualitative methods. Also they are easy to implement and are appropriate.

In these methods, bacterial cells are inoculated on nutrient agar plates over which textile samples are waiting to intimate contact. The plates are incubated in incubator at 37°C for 18–24 h and investigated for growth of bacteria directly beneath the fabrics and suddenly around the edges of the fabrics. Can not growth of bacterial directly underneath the fabric sample indicates the existence of antimicrobial activity. The zone of inhibition should not be expected if the antimicrobial agent is tightly bounded to the textile (e.g. covalently) which prevents its diffusion into the agar. If the antimicrobial agent can diffuse into the agar, a zone of inhibition becomes visible and its size ensure some indication of the potency of the antimicrobial activity or the release rate of the active agent [42].

1.9.2 Suspension Method

The süspension methods include AATCC 100-2004, JIS L 1902-2002 and SN 195924-1992. These methods provide quantitative values on the antimicrobial finishing, but are more time-consuming than agar diffusion methods [42]. Generally, a small volume (e.g. 1 ml) of bacterial inoculum in a growth media is fully absorbed into fabric samples of suitable size without leaving any free liquid. This provides intimate contact between the fabric and the bacteria. After incubating the inoculated fabrics in sealed jars at 37°C or 27°C for up to 24 h, the bacteria in the fabric are eluted and the total number is determined by serial dilution and coating on nutrient agar plates. Antimicrobial activity, expressed as percentage of reduction, is calculated by comparing the size of the initial population with that following the incubation.

Proper controls should be made at each stage. It may be important to choose a calculation equation. Because different equations can have different consequences for the same cluster [43].

It should be noted that suspension tests are often performed under artificial conditions that promote bacterial growth. The moisture in the tests is also necessary for biocide movement. Consequently, good results are often produced. This is evidence of antimicrobial activity [42,44].

1.9.3 Soil Burial Method

Soil burial tests are often used in place of true outdoor exposure to assess the resistance of textiles to mildew and rotting [39]. Siu expressed that soil burial method is very effective in (when compared to actual open air exposure of fabrics); Such as soil temperature, moisture content, soil nutrients, and other factors known to cause high variability in test results, should be interpreted carefully [45].

The samples remain buried for up to 28 days, longer for plastics and plastics. It is regarded as breaking strength or weight loss. Control samples are spoiled within approximately 7 days. It's the simplest test method. But it is long and expensive at the same time [46].

1.10 Antimicrobial Substances Used in Textile Industry

Major antibacterial substances used in textile industry; Metal and metal salts (Cu, Zn, Co, Ag, Ti, Au etc.), N-halamine, polyhexamethylenebiguanide, chitosan, peroxyacids, quaternary ammonium compound and triclosan [30]. There are important effects of chemical substances and microorganisms in medicine, industry and agriculture. These microorganisms are bacteria, fungus, algae, mold and yeast. Microorganisms are used for the purpose of eliminate deleterious organisms. Biocidal products are required to protect human and animal health. Biocides are catagorized in two groups. They are pesticides and antimicrobials. Pesticides contains fungicid, herbicides and algaecides. Antimicrobials contains includes antibiotics, antibacterial and antiviral agent [47]. Advantages / disadvantages of commonly used biocides are shown in table 1.6 [48].

Table 1.6 : Advantages and Disadvantages of Biocides [48].

Biocide	Fabric	Advantage	Disadvantage
Silver	Polyester / nylon / wool / modified cellulose	Slow release, durability	Silver can be consumed
Quarternary Amonium Compaunds	Cotton /polyester/nylon/wool	Covalent bonding, durability	Possibility of bacterial resistance
PHMB (Polyhexamethylen biguanide)	Cotton/polyester/nylon	-	Large quantities required, possible bacterial strength
Triclosan	Polyester / nylon/ polypropylene / cellulose acetate / acrylic fiber	-	Large quantities required, potential bacterial resistance ,toxic,dioxane disruption
Chitosan	Cotton/polyester/wool	-	Strength of acquisition, low durability
N-Halamine	Cotton/polyester/nylon/ wool	Development needed	Odorous due to waste chlorine
Peroxyacids	Cotton/polyester	Development needed	Low endurance

In hight doses of inhalation, nano TiO_2 can behavior as an inflammation substance and can harmful to body tissues. Also, nanoparticles can transported to other organs via the blood, but it cannot compose a crucial risk. As a result, the toxic effects of these materials should be attention [30].

Another aspect is that the antimicrobial finishing of textiles should not kill the resident flora of nonpathogenic bacteria on the skin of the wearer. The skin is composed of several bacterial genera, which are important for skin health [5,76]. Antimicrobial textiles do not change the skin flora. There is also no evidence of pathogen bacterial development [42, 49].

Textile products made of various fibers, are susceptible to growth of, pathogenic microorganisms. Increasing consumer demand for hygienic products has significantly increased the use of antimicrobial matters in textile products. Antimicrobial textile products differ in effectiveness and durability depending on the type of fabric used, the agent and the method of finishing used. However, the join to the textile surface or into the fiber limits their usability. In addiation to, the use of the textile product and washing can destroy the biocide. For these reasons, large amounts of these biocides need to be applied to textiles to effectively control bacterial growth and to sustain durability.

There are various classes of antimicrobial agents used in textile industry. These classes are not new and are used in other industries. Such as, food preservatives, disinfectants, swimming pool sanitizers and wound dressers [42].

Purwar and Joshi and recently Gao and Cranston evaluated the mechanism of action of antimicrobial agents, their activities, their application methods, and their development in antimicrobial fibers [5, 42].

1.10.1 Quaternary Ammonium Compounds (QASs)

Cationic surfactants, containing especially quaternary ammonium salts are signficant biocides. Biocides were used as antiseptic and disinfectant substance. These are active against a wide spectrum of microorganisms.

The mechanism of antimicrobial function formation is as follows. There consists interaction between the cationic ammonium group and the negatively charged cell membrane. As a result, surfactant microbial complex formed. Reduces the functions of the cell membrane and stops protein activity [50, 42, 51].

The advantages of fixed bonding to the textile surface:

1. They can behavior as a biological transporter.

2. Kills microorganisms by contact.

3. Polymer bound to the surface of the fibers is formed.

4. Strongly strengthens the durability and wash resistance of the antimicrobial agent [50].

Despite many positive features, the most important negative feature is leakage from textile materials.

There are no reactive functional groups in the structure of the quaternaryammonium salts to allow its chemical bonding to the fibers. Due to the lack of physical bonding, leaching of the QAS occurs. In addition, QASs have poor wash durability [50].

1.10.2 Triclosan

Triclosan (TCS; 2,4,40-trichloro-20-hydroxydiphenyl ether or 5-chloro-2-[2,4-dichloro-phenoxy]-phenol) (for structure, see Figure 1.3) is a biocide with a long history of use in health care and household products [52]. Ticlosan is a synthetic antibacterial and antifungal. It has broad spectrum antimicrobial properties. For this reason it is resistant to Gram positive and Gram negative bacteria. It is tasteless, odorless and bacteriostatic with high thermal stability. Triclosan is widely used in products such as soaps, detergents, fibers and plastics [53]. Today, triclosan can be found as an antimicrobial in consumer care products such as toothpaste, mouthwash and soaps [54].

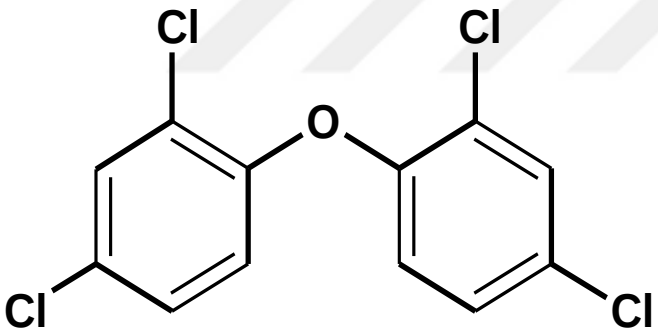


Figure 1.3 : Structure of triclosan (5-chloro-2-(2,4-dichlorophenoxy)- phenol).

1.10.3 Chitosan

Chitosan is obtained from chitin by a deacetylation processes shown in Figure 1.4 [55].

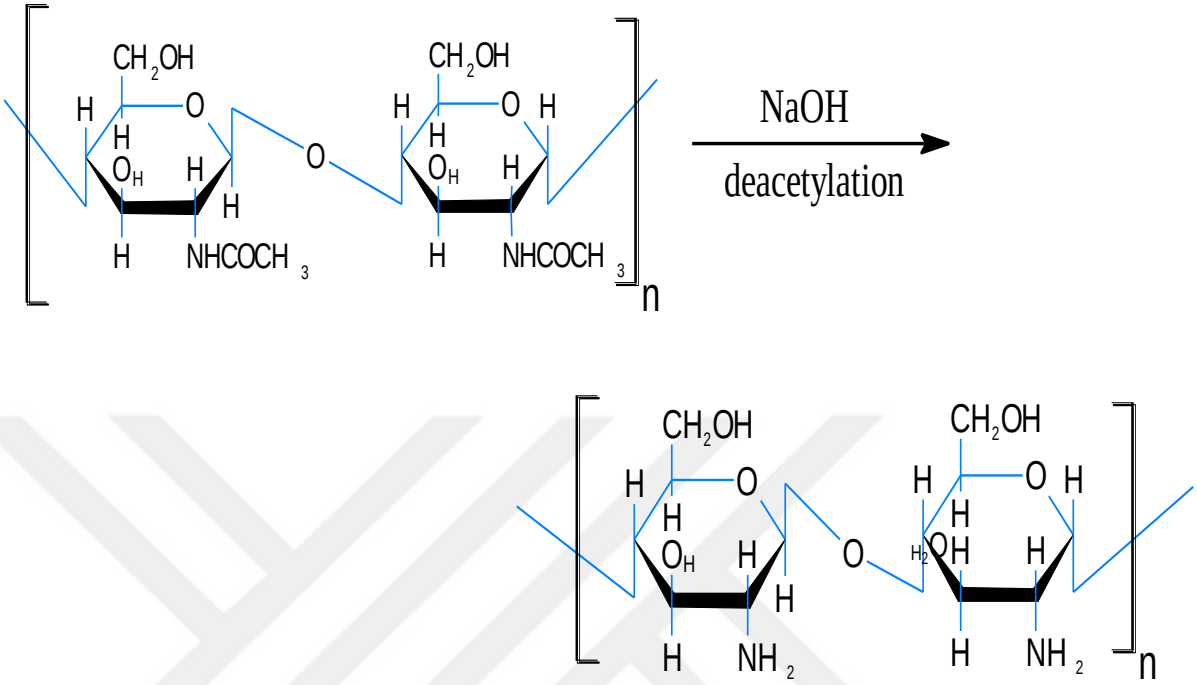


Figure 1.4 : Deacetylation process of chitin [55].

Chitosan are naturally occurring β-1,4-linked linear polysaccharides similar to cellulose as shown in Figure 1.5. But, chitosan has $–NH_2$ (amino) group. The presence of amino group in C2 position of chitosan, are provide antibacterial activity [56].

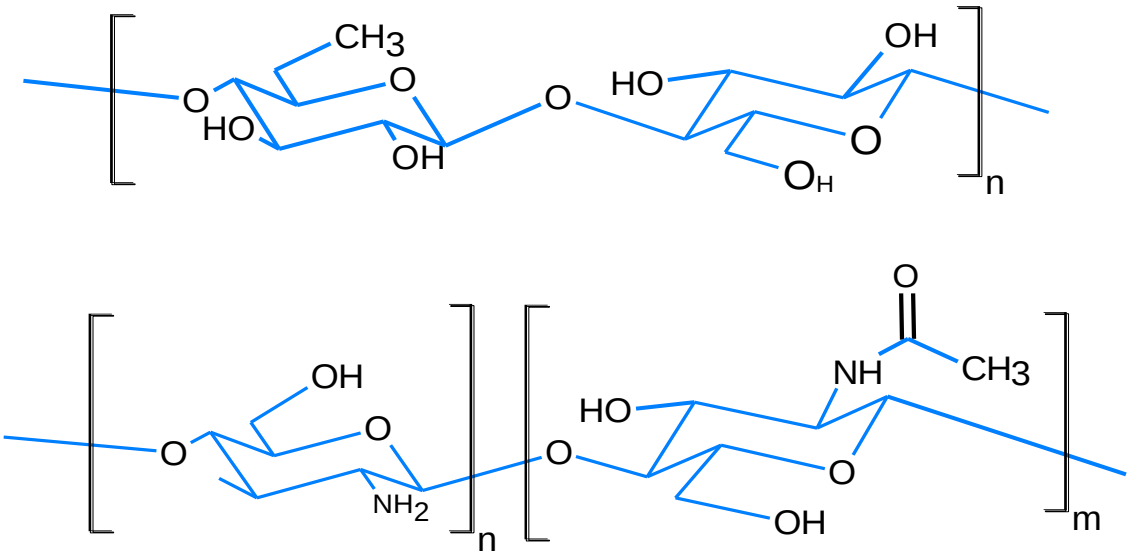


Figure 1.5 : Chemical structure of cellulose (a), chitosan (b) and chitin (c) [56].

Chitin, is the most widesperads polymer found in nature after cellulose [17]. Chitin is an amino polysaccharide that comes from the shells of shellfish [55]. The more interesting material property of chitosan compared to chitin, is due to the large variety of useful forms and commercially availiability [57].

Owing to its high biodegradability, and nontoxicity and antimicrobial properties, chitosan is widely-used as an antimicrobial agent either alone or blended with other natural polymers.Chitosan has wide spectrum of activity and high killing rate against Gram-positive and Gram-negative bacteria, but lower toxicity toward mammalian cells [58]. Chitosan exhibits good antimicrobial performance [59]. In medical textile area, they have been used as medical artificial skin, surgical sutures, artificial blood vessels, controlled drug release, contact lenses' construction, wound bandage, wound dressing, bandage, cholesterol control (fat binder), tumor inhibitor [60]. Chitosan can be used as antibacterial final material as well as it can also provide antibacterial effects directly as chitosan fibers [61,62,63]. In addition, there are various antimicrobial fibers produced from a mixture of chitosan and other fibers [64]. Examples;

1.Crabyon fibers(mixture of chitosan and viscose).

2.Chitopoly fibers (mixture of chitosan and polyisonic fiber (Fuji)) [64,2].

1.10.4 N-Halamin

N-Halamines are organic heterocyclic compounds. The nitrogen in the structure of these compounds is linked by a covalent bond to the halogen. Halogen is usually clorine. N-Halamines has a wide spectrum of bacteria, fungi and viruses. Also, these are active biocides [50].

The textile materials have been modified by co-polymerization using N-halamine. N-Halamine and its functional groups were developed by Sun, Worley et al [65]. In addition, N-halamine precursor, 3-(2,3-dihidroksipropil)-5,5-dimetilimidazolidin-2,4-dion have been synthesized by Worley et. al [66].

Since antimicrobial activity and durability are very good, N-halamide monomers were polymerized on cellulose fibers [50]. This reaction reverses from the N-Halamine bond (NCl) to the NH bond as shown in Figure1.6.

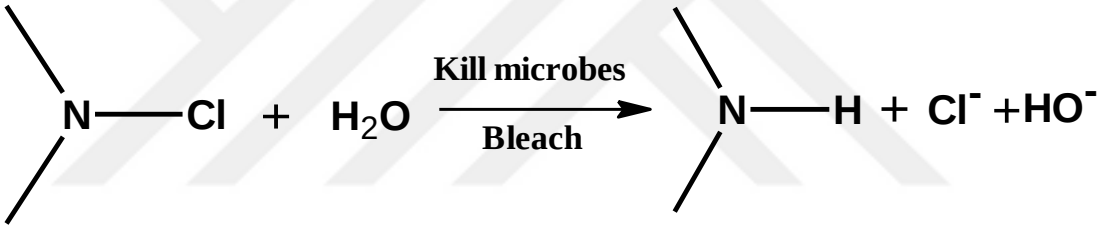


Figure 1.6 : Antimicrobial treatments with N-Halamine compounds.

Chemically, these structures work similar to chlorine bleach in killing the biological agent by oxidation via release of free halogen [67]. The antimicrobial properties are based on the electrophilic substitution of chlorine and hydrogen. Chlorine ions bind to microorganisms in aqueous media. This adversely affects enzymatic and metabolic processes. As a result, microorganisms are destroyed [50].

N-Halamine structures have gained wide attention and appreciation as biocidal agents for a variety of surfaces. N-Halamine structures i.e., NX, where X = Cl or Br have been widely studied and found suitable to be used close to human skin [67].

1.10.5 Peroxyacids

Peroxyacids are used as powerful disinfectant and renewable antimicrobial terminations [31].

Peroxyacids are used as powerful disinfectant and renewable antimicrobial terminations. As shown in Figure 1.7 peroxyacids are converted to carboxylic acid in deactivating microbes. However, these can regenerated through the reaction with an oxidant such as hydrogen peroxide [68].

Figure 1.7 : Regenerable antimicrobial treatments using peroxyacids.

Citric acid is applied to the cotton fabrics by inoculation in the padding, drying, curing process by Huang and Sun [68,69]. Then, with the oxygen bleach bath [68] or sodium perborate transformed peroxyacids [69]. Such finishing can also be applied to polyester fabrics [70]. However, antimicrobial activity is observed to decrease after several washes. [68, 69].

A popular alternative to replace or minimize the us of chlorine bleach are totally chlorine-free blenching agents commonly used in TCF is hydrogen peroxid and related peroxygen compounds. this class of bleaching agents is also referred to as oxidative bleaching agents or peroxygen bleaches. oxidative bleaching agents eliminate the environmental concerns associated with chlorine bleaches and are unlimited for use on colored or non colored fabrics.

Peroxyacids are frequently used as oxidizing agents because the perhydroxyl group in peroxyacids contains an electrophilic oxygen. In organic synthesis, these compaunds can react, for example, with alkenes, by adding this oxygen to the double bond to from oxacyclopropane through epoxidation; the other product of the reaction is a carboxylic acid.

The oxidative potential and biocidal activity of peroxyacids is particularly desirable if imparted onto fibros materials for use in antimicrobial applications [71].

1.10.6 PHMB (poly hexamethylenebiguanide)

Polybiguanides are polymeric polycationic amines that include cationic biguanide repeat units separated by hydrocarbon chain linkers of identical or dissimilar length. One of the most important antimicrobial agents among them is poly (hexamethylenebiguanide) (PHMB) with an average of 11 biguanide units. Here n_{av} is the average number of repeat unit and polybiguanide as shown Figure 1.8 [72].

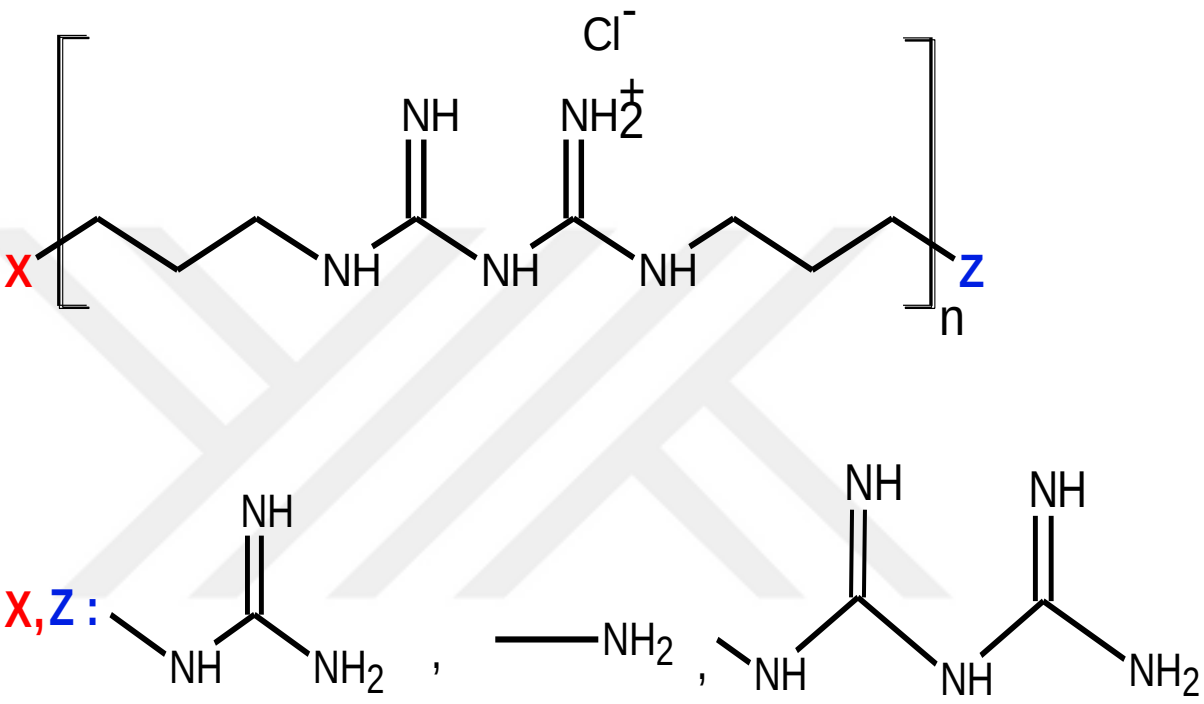


Figure 1.8 : Chemical structure of Poly(hexamethylenebiguanide) [72].

PHMB, shows much more antimicrobial activity than the monomeric or dimeric biguanides.

PHMB is widely used as an antiseptic agent of medicine in the prevention of wound infection by antibiotic resistant bacteria [50].

At lower concentrations, electrostatic interactions between PHMB and carboxylic acid groups in the cellulose dominate with a contribution to binding through hydrogen bonding; as the concentration of PHMB increases, hydrogen bonding with cellulose becomes increasingly dominant. PHMB can bind to the anionic carboxylic groups of cellulose, which are formed through oxidation of glucose rings during pretreatment processes such as bleaching and mercerizing as shown Figure 1.9 [73].

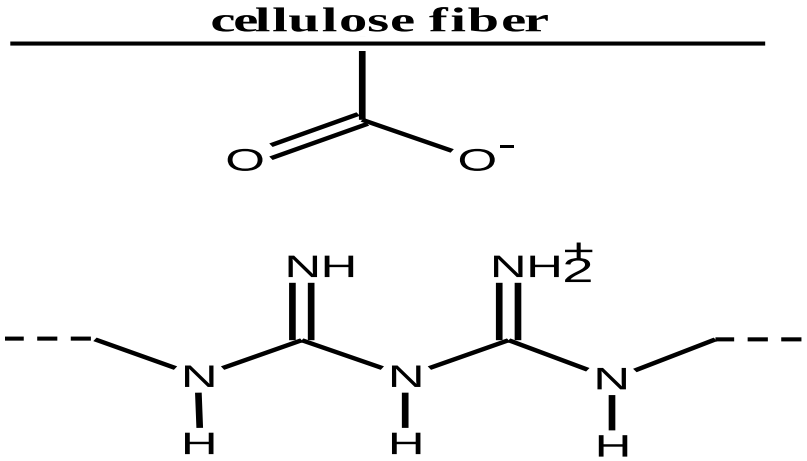


Figure 1.9 : Binding of poly (hexamethylenebiguanide) to the carboxylic group of cellulose [73].

Broxton et al. (1984) proposed that the interaction of PHMB and bacterial membrane phospholipids results in cell membrane disruption and lethal leakage of cytoplasmic materials. In 2011, was showed that electrostatic interactions are a strong factor by Yanai et al. [74].

1.10.7 Silver

The vast majority of antibacterial substances used in the textile industry work with controlled release mechanisms. Antibacterial effects can be activated by gradual and sustained release in the presence of moisture from the textile to the surface, because they are not chemically bound to the textile material.

Chemically bonded antibacterials are more resistant to washing [5]. However, in this case the binding of the antibacterial products to the textile surface or inclusion in the fabric may limit their ability to reduce their activity and the biocide amount may gradually decrease during the washing and use of the textile. For these reasons, large amounts of biocide must be applied to the textile [5].

Silver in its metallic state is inert but it reacts with the moisture in the skin and the fluid of the woundand gets ionized. The ionized silver is highly reactive, as it binds to tissue proteins and brings structural changes in the bacterial cell wall and nuclear membrane leading to cell distortion and death [48].

The explanation of silver antimicrobial mechanism can be explained as follows: Generally, metal ions destroy or pass through the cell membrane and bond to the –SH group of cellular enzymes. The consequent critical decrease of enzymatic activity causes micro-organism metabolisms change and inhibits their growth, up to the cell's death. The metal ions also catalyze the production of oxygen radicals that oxidize molecular structure of bacteria. The formation of active oxygen occurs according to chemical reaction [50].

$$H_2O + {}^1/_2\, O_2 \xrightarrow{Metal\ ion} H_2O_2 \rightarrow H_2O + (O)$$

The silver ions release of the intracellular. Thus, it increases bactericidal activity and inhibits the respiratory chain. Antimicroabial agent does not direct contact with bacteria. Because this mechanism with produced active oxygen diffuses from wool fabric to the surrounding [50].

For centuries silver has been in use for the treatment of burns and chronic wounds. As early as 1000 B.C. silver was used to make water potable. Silver nitrate was used in its solid form and was known by different terms like, "Lunar caustic" in English, "Lapis infernale" in Latin and "Pierre infernale" in French [75].

In 1700, silver nitrate was used for the treatment of venereal diseases, fistulae from salivary glands, and bone and perianal abscesses. In 1968, silver nitrate was combined with sulfonamide to form silver sulfadazine cream, which served as a broad-spectrum antibacterial agent and was used for the treatment of burns. Silver sulfadazine is effective against bacteria like E. coli, S. aureus, Klebsiella sp., Pseudomonas sp. It also possesses some antifungal and antiviral activities [75]. Silver sulfadazine works as a broad-spectrum antibiotic. It is used especially for the treatment of burn wounds [75].

In literature, it is pointed out that silver is skin friendly and does not cause skin irritation [76].

The ancient Phoenicians, Greeks, Romans, Egyptians, and others also were recorded to have used silver in one form or another to preserve food and water, and this was practiced through World War II. The application of silver plates to achieve better wound healing was used by the Macedonians, perhaps the first at- tempt to prevent or treat surgical infections. Hippocrates used silver preparations for the treatment of ulcers and to promote wound healing. It is likely that silver nitrate also was used

medically because it was mentioned in a pharmacopeia pub- lished in Rome in 69 B.C.E [77, 78]. By 1800, there was wide acceptance that wine, water, milk, and vinegar stayed pure for longer periods of time when stored in silver vessels. Silver nitrate also was used successfully to treat skin ulcers, compound fractures, and suppurat- ing wounds, well before the time of Lister. One of the seminal contributions to the medical uses of silver was by Doctor J. Marion Sims in 1852 [79,78].

In the 1880s by Doctor Carl Siegmund Franz Crede, a German, who pioneered the use of silver nitrate eye drops to prevent ophthalmia neonatorium (gonorrheal ophthalmia) in newborn infants [80,78]. He first used a 2% solution, but this was reduced subsequently to a 1% solution because of the irritation the higher concentration caused. This was a highly effective therapy, reducing the incidence of ophthalmia neonatorium from 7.8% to 0.13% in 13 years. Because of the success of this method, the employment of silver nitrate eye drops in newborn infants was widely accepted throughout the world, and in numerous countries, this therapy was mandated by law and persisted until after the introduction of effective antibiotics [78].

Silver has been in use sİnce time immemorial in the form of metallic silver, silver nitrate, silver sulfadiazine for the treatment of burns, wounds and several bacterial infections [75].

Different types of nanomaterials like copper, zinc, titanium, magnesium, gold, alginate and silver have come up but silver have proved to be most effective as it has good antimicrobial efficacy against bacteria, viruses and other eukaryotic micro-organisms [75].

The silver nanoparticles show efficient antimicrobial property compared to other convectianal silver ions due to their extremely large surface area, but there are many questions about the toxicity and reliability of nanosized silver particles [75,81].

In 1997, Liau et al., investigated the effect of silver ions on amino acids containing no thiol (-SH) groups [81].

A morphological mutation of silver ions on gram-positive S. aureus and gram-negative E. coli bacteria was investigated by Feng et al, in 2000 [82]. $AgNO_3$ was used as the ion source in the study. It has been shown that Gram-positive S. aureus

may exhibit better resistance to silver ions due to its thick cell wall as a typical positive bacteria. In addition, it has been reported that DNA, which can copy itself only in its free state, turns into a more dense form within the cell, demonstrated that DNA has lost the ability to replicate itself [82].

In 2005. Holt et. al., Electrochemical techniques were used to study the behavior of Escherichia coli on the addition of $AgNO_3$. Respiration in the presence of glucose was measured using a Clark ultramicroelectrode to determine the oxygen concentration as a function of time. The rate of respiration increased initially upon the addition of silver(I) because of the uncoupling of the respiratory chain, followed by cessation of respiration. The toxicity of $AgNO_3$, as determined by the time until respiration ceased, increased in the absence of glucose and in the presence of K^+ [83].

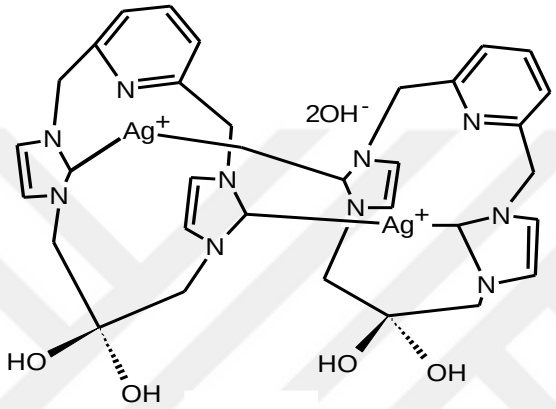
In 2010, Li et. al., The antibacterial activity and acting mechanism of silver nanoparticles on Escherichia coli ATCC 8739 were investigated in this study by analyzing the growth, permeability, and morphology of the bacterial cells following treatment with silver nanoparticles.Besides, Kim et al. found that Ag+ interacted with thiol (–SH) group of cysteine by replacing the hydrogen atom to form –S–Ag, thus hindering the enzymatic function of affected protein to inhibit growth of E.coli. [81].

The commercial antibacterial termination agent has been investigated in terms of washing resistance and the physical properties of cotton fabrics by Üreyen et.al. All fabric samples were washed 40 times. The physical properties and antibacterial activity of the treated and untreated fabrics were tested after washing every 10 cycles. Good antibacterial activity could be achieved even after 40 launderings with many different antibacterial agents. However, the antibacterial activity of the samples treated with different agents changed. The results show that silver had a strong antibacterial activity even at a low concentrationn [8].

Yeo et. al., was prepared polypropylene/silver compounds by melt compounding using a general counter-rotating twinscrew mixer and was produced nanocomposite fibers. All of the compounds incorporating silver I exhibited perfect antibacterial behavior, but poylpropylene compounds low antibacterial activity [84].

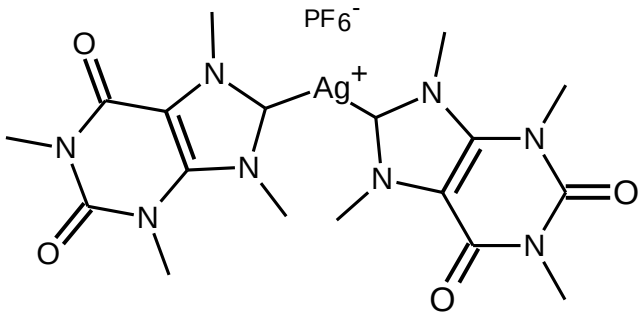
Son et al., was developed a method for the production of silver nanoparticle containing ultra thin antimicrobial acetate fibers by electrospinning by adding silver nitrate to the cellulose acetate (CA) solution [85].

Youngs et. al. firstly introduced application of Ag-NHC complex to pharmacutical industry. In their study, compare to aqueous solution of silver, effectivity of the complex I (at below) is found to be longer. Moreover, caffeine Ag(I)-NHC complexes (II-III) have been indicated effective antimicrobial activity against patogens in lung in cystic fibrosis patients [86].

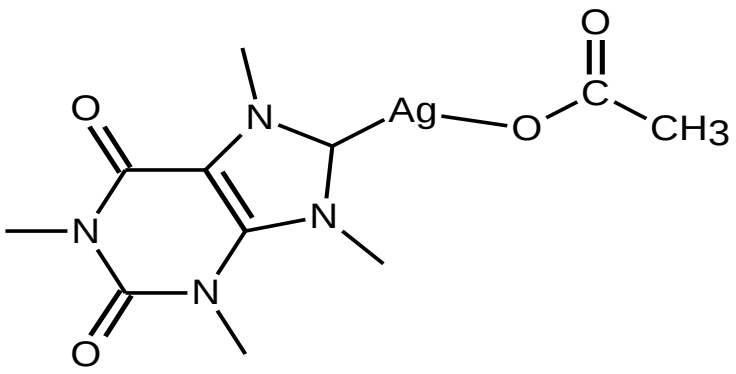


I

Figure 1.10 : The Complex I.



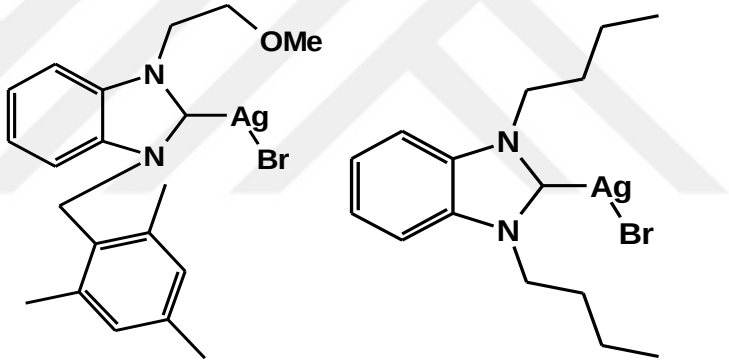
II



III

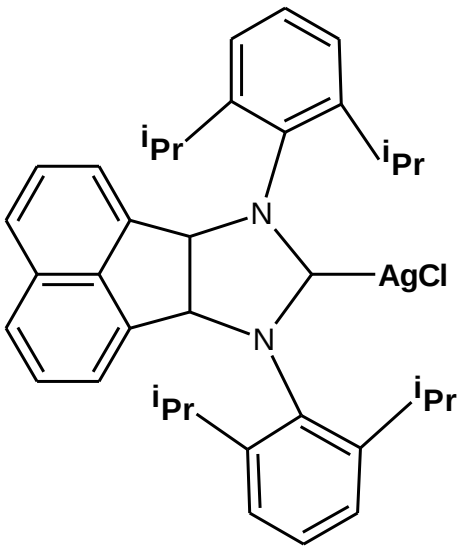
Figure 1.11 : Caffeine Ag(I)-NHC Complexes (II-III).

In 2010, İ. Özdemir et. al. was synthesized silver(I) NHC complexes (IV,V) and examined their activity against gram positive, gram negative bacteria and fungi [87]. In 2011, Cowley et. al. was synthesized Ag-NHC complexes (VI, VII) and achieved similar results [88

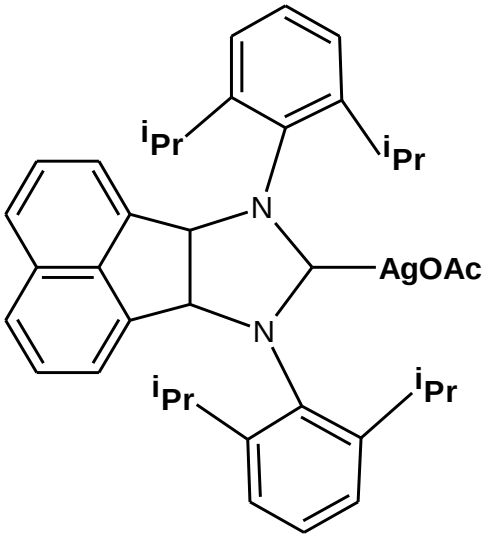


IV V

Figure 1.12 : Silver(I) NHC Complexes (IV,V).



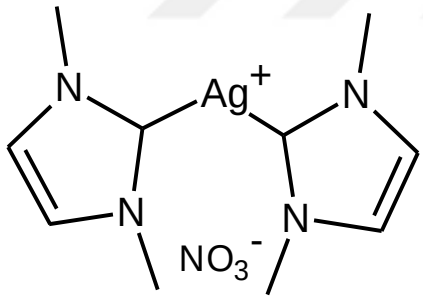
VI



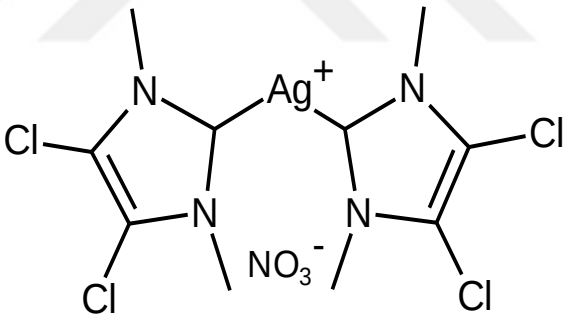
VII

Figure 1.13 : Ag-NHC complexes (VI, VII).

In 2011, silver(I) NHC comlexes (VIII,IX) has antimicrobial properties and this complexes anti cancer properties was also reported by Sicilliano T. Et al [89].



VIII



IX

Figure 1.14 : Silver(I) NHC Comlexes (VIII,IX).

Long chain alkyl group, quarterner amonium group and substutie chloro group compounds have been demonstrated to be the most efficacious antimicrobials because of their long-term stabilities, nontoxicities to the environment, and broad spectra of biocidal activities. This goups gives good results when including anticacterial mechanism. A lengthy alkyl group is generally required for penetration of the outer cell membrane. On the other hand, quaternary ammonium groups are

adsorbed onto phosphate containing cell walls of bacteria through an ionic interaction. Then, quats penetrate the cell wall and are attracted to the cytoplasmic membrane, resulting in leakage of intracellular components. While halogen containing structures are reported to have antibacterial effects [90].

As a result, silver is now used in a large number of commercial antimicrobial synthetic fibers and yarns [5].

The commercially available silver complexes show a rapid release of Ag in aqueous media due to the having ionic structure. Therefore, they have efficient but short-term antibacterial activity. In this works, N-heterocyclic carbene (NHC) complexes having the ability to gradually leave Ag ions to solution will be synthesized. In addition, those Ag-NHC complexes will be immobilized on wool fabric so that it has specific characteristics such as washing durability, excellent antibacterial property as well as stability to darkening under illumination.

2. EXPERIMENTAL

Imidazole, 1-bromo-3-chloropropane, bromobutane, bromooctane, bromododecyl, bromohexadecan were purchased from Alfa Aesar and Sigma-Aldrich; dichlorometane, chloroform, diethylether, hegzane, acetone, dimethylsulphoxide, CHT Felosan LFA: Wetting, CHT TUBIVIS VP 681: Thickeners, CHT COTOBLANC PCS: Washing material, soapwere purchased from Merck.

^{1}H-NMR and ^{13}C-NMR spectra were recorded on Bruker 400MHz Ultrashield TM spectrometer , Varian Mercury AS 400MHz spectrometer and Varian 600 MHz 297 K. As solvent $CDCl_3$, MeOD or DMSO was employed. The chemical shifts (&) are given in units of billion (ppm) and the coupling constants (J) in hertz. The Infrared Spectrum was measured using the Thermo Nicolet iS5 FTIR system and the ATR id5 sampling accessory. J values are given in Hz. IR spectra were obtained Thermo Nicolet İS5 ATR spectrometer.

Vertical Fulard (Brand: Rapid, Model: PA1) for working with the impregnation method in the cloth haulage experiments; (Brand: Rapid, Model: H240F) and Laboratory Type Dryer (Brand: Rapid, Model: R-5) were used for drying the fabrics.

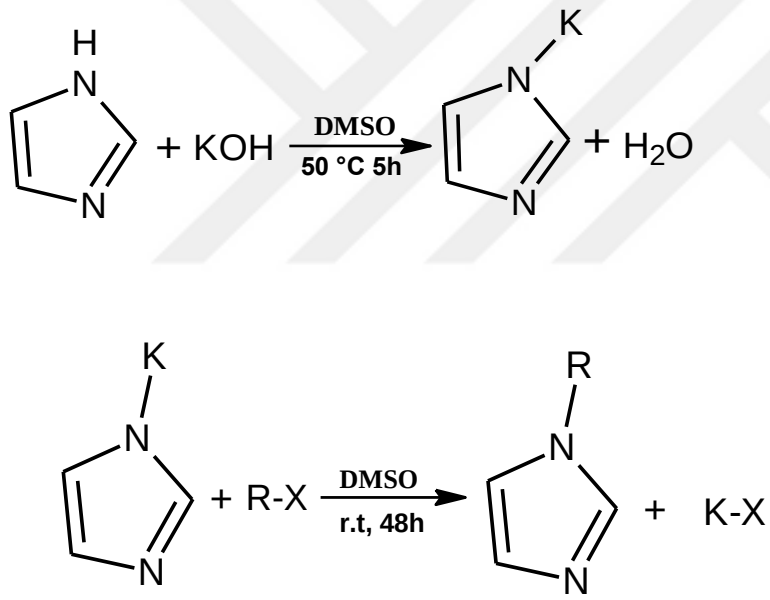
Figure 2.1 : Laboratory Type Dyeing Machine, Brand: Rapid, Model: H240F.

Figure 2.2 : Laboratory Type Dryer: Brand: Rapid, Model: R-5.

SEM-EDX data were measured at Selçuk University and SemEdx analyzes were performed using the Carl Zeiss EVO LS10 model device. ICP-MS datas were measured in İzmir Institute of Technology.

2.1 Synthesis of Derivatives of Imidazole

Imidazole and KOH were dissolved in DMSO and stirred at room temperature for 5 hours. Alkyl halide was added. Mixture was stirred at 50 ^{o}C for 48 h. After then, the reaction mixture was diluted with water and extracted with $CHCl_3$. The solvent was seperated from the organic fractions affording the product. The solvent was removed and the product washed with hexane and diethylether. After , solvents were evaported under vacuum and product formed.



R: ethyl: **1a**, buthyl: **1b**, octyl: **1c**, dodecyl: **1d**, hexadecyl: **1e**

X: I, Br

Figure 2.3 : Synthesis of Imidazol Derivatives of 1th Type.

2.1.1 Synthesis of 1-ethyl-1H-imidazole (1a)

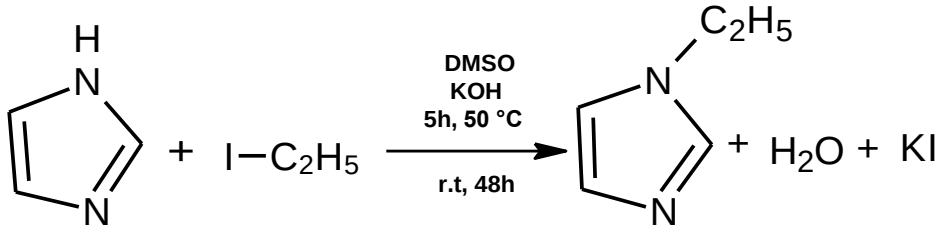


Figure 2.4 : Synthesis of 1-ethyl-1*H*-imidazole.

Imidazole (4.00g; 58.8mmol) and KOH (4.94g; 88.2mmol) were dissolved in DMSO (10mL) and stirred at room temperature for 5 hours. Iodoethane (10.1g; 64.7mmol) was added. Mixture was stirred at 50^{o}C for 48 hours. After then, the reaction mixture was diluted with water (500mL) and extracted with $CHCl_3$ (5x25mL). The solvent was seperated from the organic fractions affording the product. The solvent was removed and the product washed with hexane and diethylether. After, solvents were evaported under vacuum and light yellow oil formed. Yield % 46 ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 1.42 (t, J=6.0 Hz, 3 H); 3.95 (q, J= 8.0 Hz, 2 H); 6.89 (s,1 H,); 7.01 (s, 1 H); 7.45 (s, 1 H). FT-IR (cm^{-1}): 3111, 2955, 2933, 2873, 1666, 1508, 1461, 1228, 1107, 1078, 1030, 915, 812, 733, 654, 624.

2.1.2 Synthesis of 1-butyl-1H-imidazole (1b)

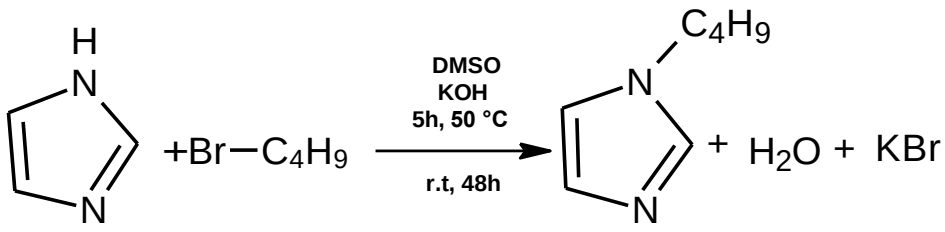


Figure 2.5 : Synthesis of 1-butyl-1*H*-imidazole.

This product was prepared analogously to **1a** with imidazole (4.00g; 58.8mmol), KOH (4,94g; 88.2mmol) and bromobuthane (11.9g; 64.7mmol) as the starting materials. Light orange oil was occured. Yield % 51 ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 0.90 (t, J=8.0 Hz, 3 H); 1.24-1.31 (m, 2 H); 1.68-1.75 (m, 2 H,); 3.88 (t, J= 6.0 Hz, 2 H), 6.86 (s, 1 H), 7.00 (s, 1 H); 7.41 (s, 1 H). FT-IR (cm^{-1}): 3110, 2958, 2933, 2873, 1668, 1508, 1461, 1228, 1107, 1078, 1029, 915, 812, 733, 664, 624.

2.1.3 Synthesis of 1-octyl-1H-imidazole (1c)

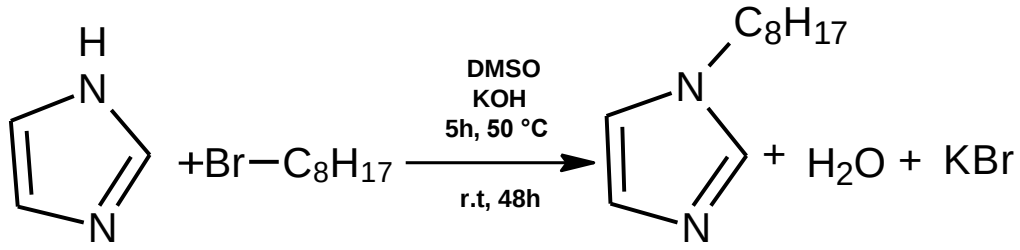


Figure 2.6 : Synthesis of 1-octyl-1*H*-imidazole.

This product was prepared analogously to **1a** with imidazole (4.00g; 58.8mmol), KOH (4.94g; 88.2mmol) and bromooctane (12.49g; 64.7mmol) as the starting materials. Orange oil was occured. Yield % 62 ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 0.84 (t, J=6.0 Hz, 3 H); 1.23-1.26 (m, 10 H); 1.70-1.77 (m, 2 H); 3.88 (t, J= 8.0 Hz, 2 H), 6.86 (s, 1 H), 7.01 (s, 1 H); 7.42 (s, 1 H). FT-IR (cm^{-1}): 3109, 2924, 2854, 1680, 1507, 1455, 1375, 1282, 1228, 1107, 1077, 1029, 914, 906, 806, 725, 663, 624.

2.1.4 Synthesis of 1-dodecyl-1H-imidazole (1d)

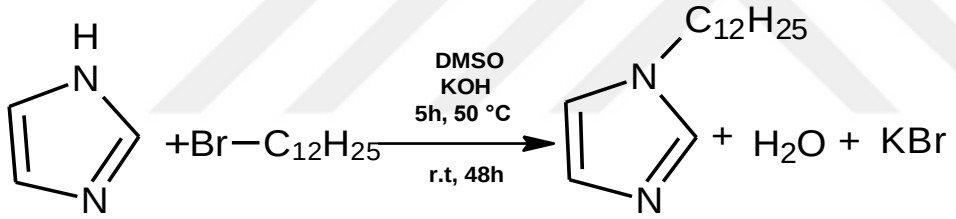


Figure 2.7 : Synthesis of 1-dodecyl-1*H*-imidazole.

This product was prepared analogously to **1a** with imidazole (4.00g; 58.8mmol), KOH (4.94g; 88.2 mmol) and bromododecyl (16.13g; 64.7mmol) as the starting materials. Dark orange oil was occured. Yield % 65 ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 0.86 (t, J=8.0 Hz, 3 H); 1.24-1.28 (m, 18 H); 1.71-1.78 (m, 2 H); 3.89 (t, J= 6.0 Hz, 2 H), 6.87 (s, 1 H), 7.03 (s, 1 H); 7.43 (s, 1 H). FT-IR (cm^{-1}): 3316, 2955, 2916, 2847, 1645, 1619, 1570, 1505, 1463, 1388, 1340, 1265, 1239, 1222, 1137, 1074, 1015, 850, 763, 721, 663.

2.1.5 Synthesis of 1-hexadecyl-1H-imidazole (1e)

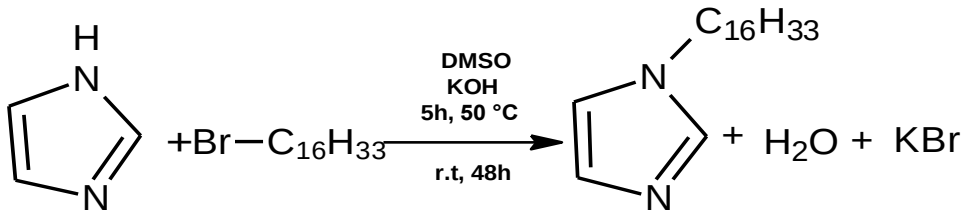


Figure 2.8 : Synthesis of 1-hexadecyl-1H-imidazole.

This product was prepared analogously to **1a** with imidazole (4.00g; 58.8mmol), KOH (4.94g; 88.2mmol) and bromohexadecane (19.75g; 64.7mmol) as the starting materials. White solide was occured.Yield % 58 ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 0.86 (t, J=6.0 Hz, 3 H); 1.24-1.27 (m, 26 H); 1.75 (t, J=6.0 Hz, 2 H); 3.89 (t, J= 6.0 Hz, 2 H), 6.87 (s, 1 H), 7.01 (s, 1 H); 7.43 (s, 1 H). FT-IR (cm^{-1}): 3115, 2954, 2916, 2848, 1660, 1509, 1472, 1375, 1281, 1229, 1109, 1082, 1027, 917, 907, 815, 784, 730, 718, 661, 631.

2.2 Synthesis Of Imidazolium Salts

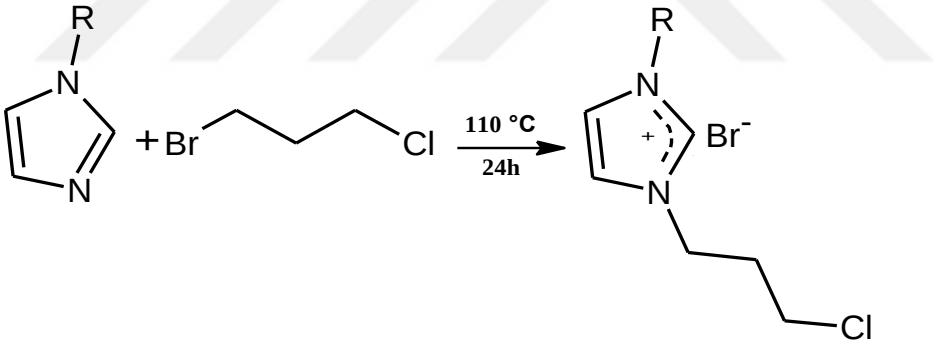


Figure 2.9 : Synthesis Of Imidazolium Salts.

Imidazol derivatives of 1th type and 1-bromo-3-chloropropane stirred at 110^{o}C for 24 h. Product was washed with diethylether and recrytalized from dichloromethane / diethylether. The solvent was evaporated under vaccum product was obtained.

2.2.1 Synthesis of 3-(3-bromopropyl)-3-chloro-1-ethyl-1H-3λ^5-imidazole (2a)

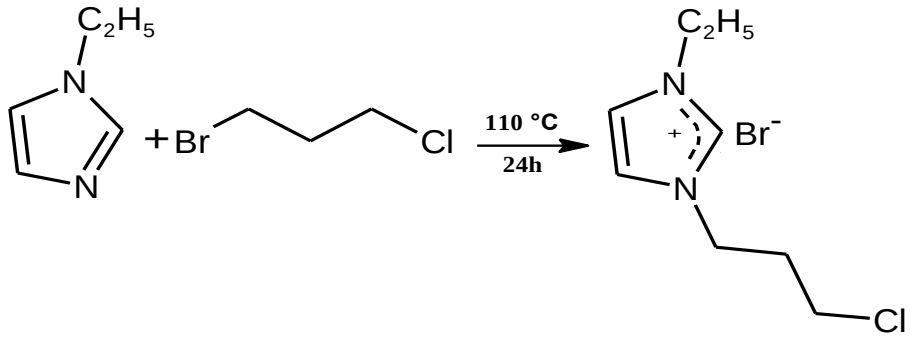


Figure 2.10 : Synthesis of 3-(3-bromopropyl)-3-chloro-1-ethyl-1H-3λ^5-imidazole.

1a (3g) and 1-bromo-3-chloropropane (5.4g) stirred at 110 ^{o}C for 24 hours. Product was washed with diethylether (10mL) and recrytalized from dichloromethane/diethylether. The solvent was evaporated under vaccum and yellow oil was obtained. Yield: % 71. ^{1}H NMR (400 MHz, D_2O, δ ppm: 9.74 (s, 1H); 7.93 (s, 1H); 7.69 (s, 1H); 4.63(m, 4H); 2.05 (t, 1H); 1.69 (t, 3H, J: 8 Hz). FT-IR (cm-1) 2982, 1551, 1448, 1147, 801, 617.

2.2.2 Synthesis of 3-(3-bromopropyl)-3-chloro-1-butyl-1H-3λ^5-imidazole (2b)

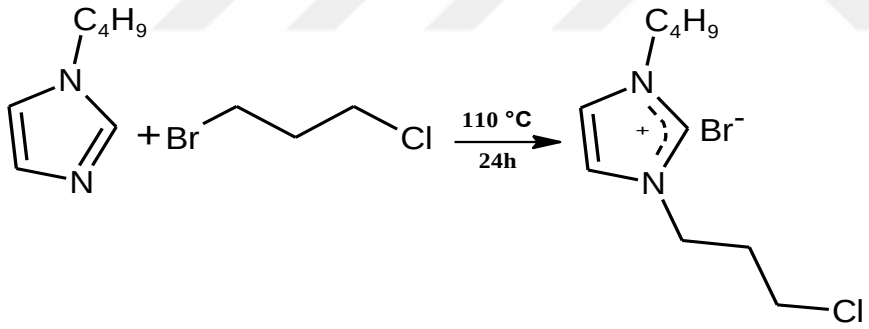


Figure 2.11 : Synthesis of 3-(3-bromopropyl)-3-chloro-1-butyl-1H-3λ^5-imidazole.

This product was prepared analogously to **2a** with **1b** (3g) and 1-bromo-3-chloropropane (4.2g) as the starting materials. Brown oil was obtained. Yield: % 88. ^{1}H-NMR (400MHz, $CDCl_3$): δ= 10.09 (s, 1H); 8.16 (s,1H); 7.37 (s, 1H); 4.63 (t, 2H, J: 6.0 Hz); 4.22 (t, 2H, J: 8.0 Hz); 2.77 (m, 1H);1.83 (m, 2H); 1.30 (m, 2H); 0.87 (m, 5H). ^{13}C-NMR (100MHz, $CDCl_3$): 136.6, 123.8, 121.5, 50.5, 46.3, 29.5, 29.3, 26.0, 22.6, 14.5. FT-IR (cm^{-1}): 3137, 3077, 2959, 2872, 1563, 1455, 1338, 1113, 751, 634.

2.2.3 Synthesis of 3-(3-bromopropyl)-3-chloro-1-octyl-1H-3λ^5-imidazole (2c)

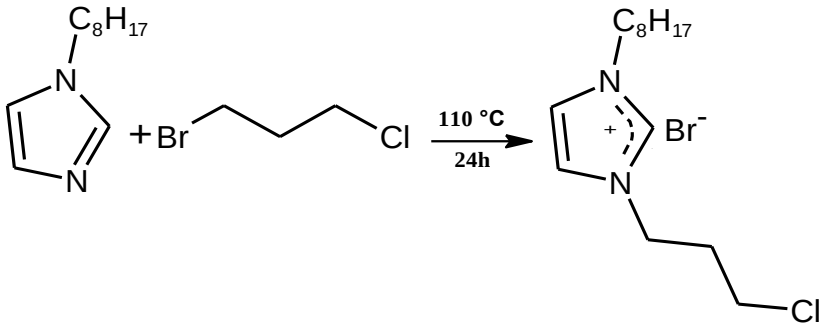


Figure 2.12 : Synthesis of 3-(3-bromopropyl)-3-chloro-1-octyl-1H-3λ^5-imidazole.

This product was prepared analogously to **2a** with **1c** (3g) and 1-bromo-3-chloropropane (2.9) as the starting materials. Brown oil was obtained.Yield: %89. ^{1}H-NMR (400MHz, $CDCl_3$): δ= (in DMSO): 9.40 (s,1H); 7.84 (s, 1H); 7.66 (s, 1H); 4.25 (m, 4H); 2.41 (m, 1H); 1.77 (m, 2H); 1.22-1.24 (m, 6H); 0.82 (t, 3 H, J: 6.0 Hz). ^{13}C-NMR (100MHz, $CDCl_3$): 142.5, 125.1, 123.6, 50.2, 46.3, 29.5, 29.3, 26.0, 22.6, 14.5. FT-IR (cm^{-1}): 3137, 3077, 2924, 2855, 1563, 1579, 1455, 1338, 1161, 749, 634.

2.2.4 Synthesis of 3-(3-bromopropyl)-3-chloro-1-dodecyl-1H-3λ^5-imidazole (2d)

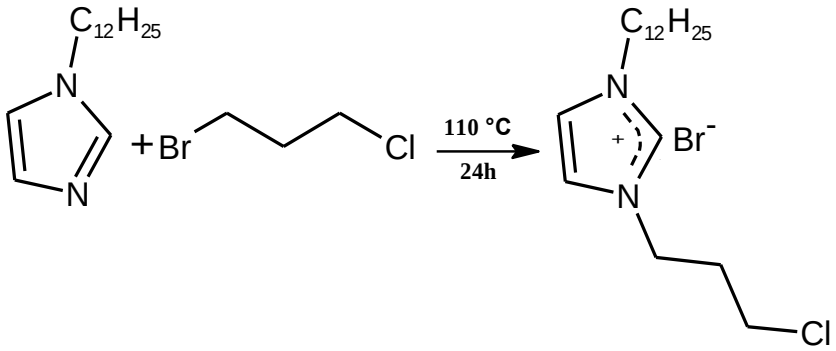


Figure 2.13 : Synthesis of 3-(3-bromopropyl)-3-chloro-1-dodecyl-1H-3λ^5-imidazole.

This product was prepared analogously to **2a** with **1d** (3g) and 1-bromo-3-chloropropane (2.2g) as the starting materials. Oragnge oil was obtained. Yield: %86. ^{1}H-NMR (400 MHz, MeOD,, δ ppm): 10.19 (s, 1H, NCHN); 8.22 (s, 1H, HCCH); 7.26 (s, 1H, HCCH); 4.68 (t, 2H, $NCH_2C_2H_4Cl$); 4.21 (t, 2H, NCH_2-$C_{11}H_{23}$, J: 8.0 Hz); 2.84 (m, 1H, $NC_2H_4CH_2Cl$); 1.86 (m, 2H, $NCH_2CH_2CH_2Cl$), 1.20-1.28 (m, 20H, $NCH_2C_{10}H_{20}CH_3$); 0.82 (t, 3H, $NC_{11}H_{22}CH_3$, J:6.0 Hz). ^{13}C-NMR: 136.4,

123.8, 121.6, 50.2, 46.7, 31.9, 31.1, 30.1, 29.6, 29.5, 29.4, 29.3, 29.0, 26.3, 22.6, 14.1. FT-IR (cm^{-1}): 3077, 2921, 2852, 1564, 1465, 1162, 721, 634.

2.2.5 Synthesis of 3-(3-bromopropyl)-3-chloro-1-hexadecyl-1H-3λ^5-imidazole (2e)

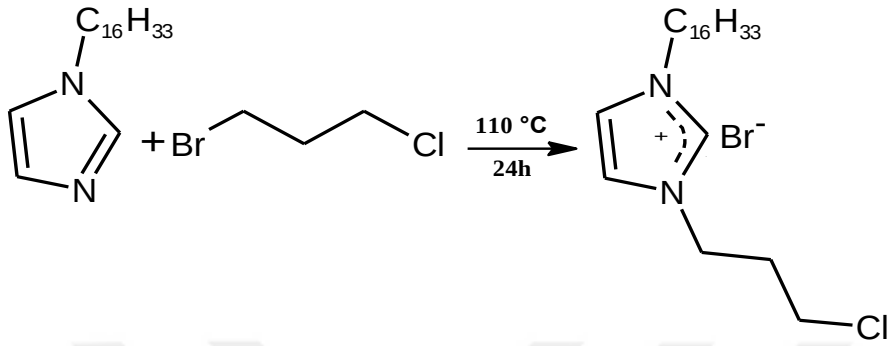


Figure 2.14 : Synthesis of 3-(3-bromopropyl)-3-chloro-1-hexadecyl-1H-3λ^5-imidazole.

This product was prepared analogously to **2a** with **1e** (3g) and 1-bromo-3-chloropropane (1.8g) as the starting materials. White solid was obtained. Yield: % 78. ^{1}H-NMR (400MHz, $CDCl_3$) δ 10.09 (s, 1H); 8.23 (s, 1H); 7.23 (s, 1H); 4.70 (t, 2H, J: 8.0 Hz); 4.21 (t, 2H, J: 8.0 Hz); 2.85 (m, 1H); 1.88 (m, 2H); 1.22-1.30 (m, 28 H); 0.85 (t, 3H, J: 8.0 Hz). ^{13}C-NMR ($CDCl_3$, δ): 136.4, 123.8, 121.5, 50.2, 46.7, 31.9, 30.1, 29.7, 29.6, 29.6, 29.6, 29.5, 29.4, 29.3, 29.0, 26.3, 22.6, 14.1. IR (cm^{-1}): 2954, 2915, 2849, 1562, 1465, 1375, 1228, 1109, 1083, 816, 784, 718.

2.3 Synthesis of Ag Complexes

Imidazol derivatives of 2th type was dissolved in dichloromethane. Ag_2O were added. The mixture was stirred at room temperature for 48 h. Excessive silver oxide was collapsed when of the mixture. The obtained mixture was filtered and washed with ether. The solvent was evaporated under vacuum and product was occured.

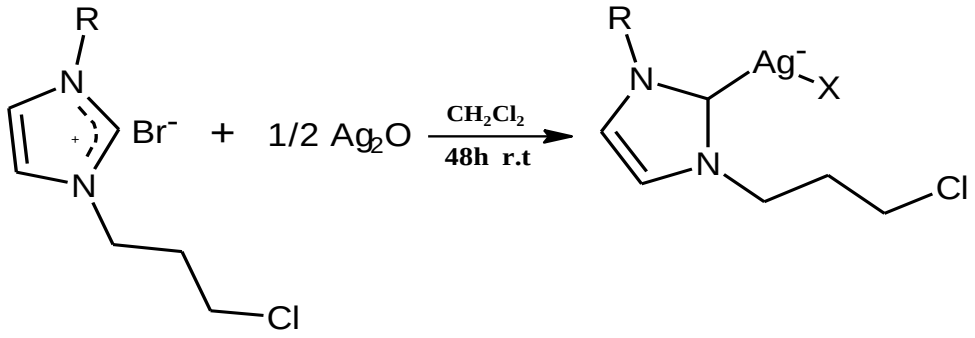


Figure 2.15 : Synthesis of Ag Complexes.

2.3.1 Synthesis of [1-ehtyl-3-(3-chloropropyl)-1H-imidazol-3-ium-2-yl]Silver Salt (3a)

2a (3 g) was dissolved in dichloromethane. Ag_2O (1.4g) were added. The mixture was stirred at room temperature for 48 h. Excessive silver oxide was collapsed when of the mixture. The obtained mixture was filtered and washed with ether. The solvent was evaporated under vacuum and white product was occured. Yield: % 46. ^{1}H-NMR (400MHz, $CDCl_3$): δ= 7.77 (s, 1H); 7.52(s, 1H); 4.06 (m, 4H); 2.47 (m, 1H); 1.42 (t, 2H, J: 6.0 Hz); 1.31 (q, 3H).

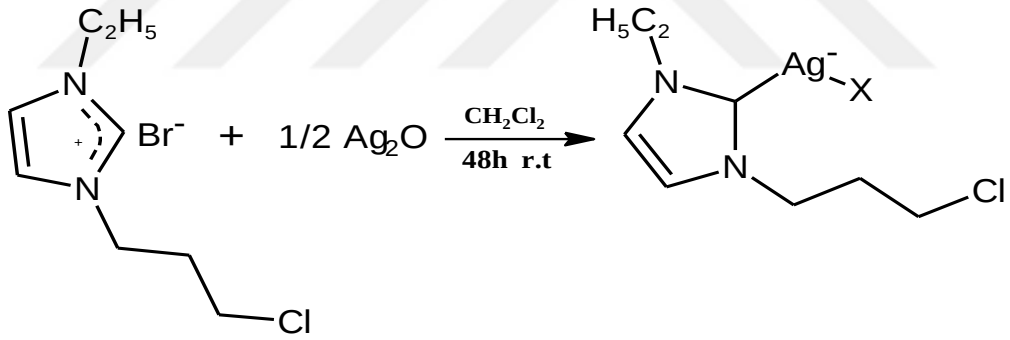


Figure 2.16 : Synthesis of [1-ehtyl-3-(3-chloropropyl)-1H-imidazol-3-ium-2-yl]Silver Salt.

2.3.2 Synthesis of [1-butyl-3-(3-chloropropyl)-1H-imidazol-3-ium-2-yl]silver salt (3b)

2b (3g) was dissolved in dichloromethane Ag_2O (1.2g) were added. The mixture was stirred at room temperature for 48 hours. The optained mixture was filtred and washed with ether. The solvent was evaporated under vacuum and brown product was occured. Yield: %86. ^{1}H-NMR (400MHz, $CDCl_3$): δ= 7.21 (s, 1H), 7.05 (s, 1H); 4.20 (t, 3H, J: 4.0 Hz); 4.12 (t, 3H, J: 4.0 Hz); 3.47 (m, 1H); 1.77 (m, 2H); 1.20 (m, 4H); 0.92 (t, 3H, J: 8.0 Hz). ^{13}C-NMR ($CDCl_3$, δ):123.1, 120.5, 51.5, 47.5, 42,38,

34.5, 32.8, 19.0, 13.5. FT-IR, (cm^{-1}) :3094, 2960, 2871, 1563, 1455, 1417, 1107, 804, 692.

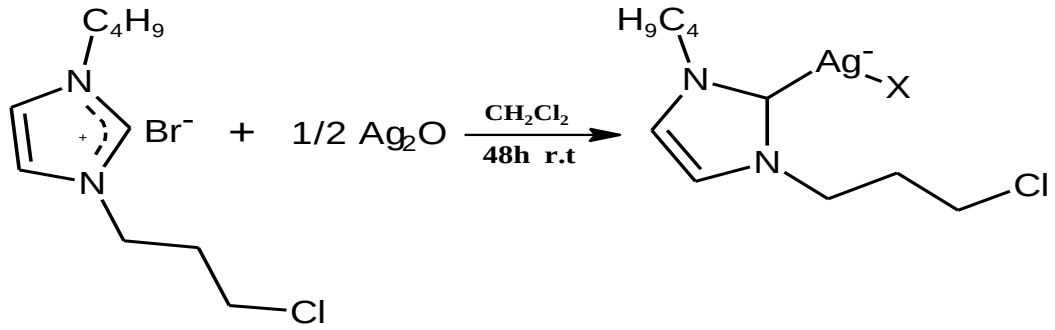


Figure 2.17 : Synthesis of [1-butyl-3-(3-chloropropyl)-1H-imidazol-3-ium-2-yl]Silver Salt

2.3.3 Synthesis of [1-octyl-3-(3-chloropropyl)-1H-imidazol-3-ium-2-yl]Silver Salt (3c)

2c (3g) was dissolved in dichloromethane Ag_2O (34mg) were added. The mixture was stirred at room temperature for 48 hours. The optained mixture was filtred and washed with ether.

The solvent was evaporated under vacuum and grey product was occured. Yield: % 92. ^{1}H-NMR (400MHz, $CDCl_3$): δ= 8.18 (s, 1H); 7.22 (s, 1H); 4.26 (t, 2H, J: 4.0 Hz); 4.08 (t, 2H, J: 4.0 Hz); 1.88 (m, 1H); 1.19-1.30 (m, 8 H); 0.86 (t, 3H, J: 6.0 Hz). FT-IR, (cm^{-1}) : 2935, 2858, 1563, 1455, 1417, 1107, 802, 693.

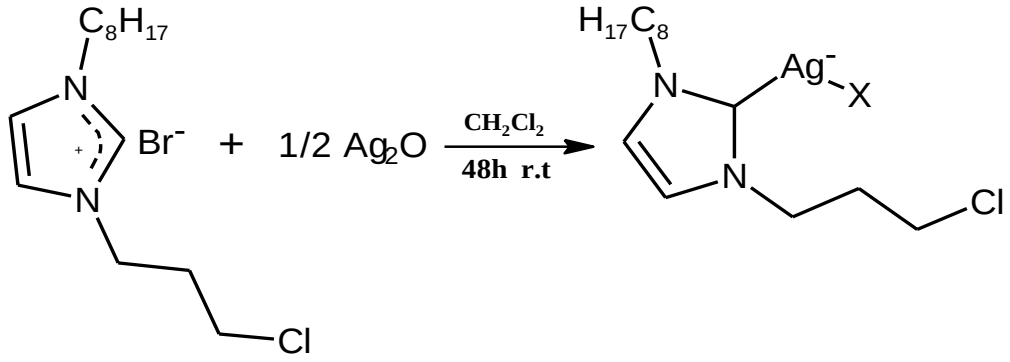


Figure 2.18 : Synthesis of [1-octyl-3-(3-chloropropyl)-1H-imidazol-3-ium-2-yl]Silver Salt.

2.3.4 Synthesis of [1-octyl-3-(3-chloropropyl)-1H-imidazol-3-ium-2-yl]Silver Salt (3d)

2d (3g) was dissolved in dichloromethane Ag_2O (881mg) were added. The mixture was stirred at room temperature for 48 h. The optained mixture was filtred and washed with ether. The solvent was evaporated under vacuum and dark brown product was occured. Yield: %78. ^{1}H-NMR (400MHz, $CDCl_3$): δ= 7.44 (s, 1H); 7.05 (s, 1H); 4.21 (t, 2H); 4.03 (t, 2H); 2.51 (m, 1H); 1.78 (m, 2H); 1.31-1.22 (m, 20H); 0.85 (t, 3H, J:4.0 Hz). FT-IR, (cm^{-1}) : 2920, 2848, 1462, 1208, 726, 659.

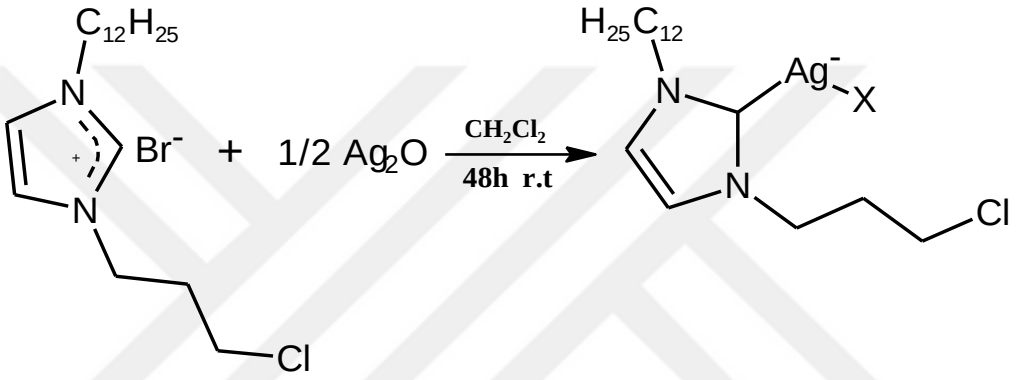


Figure 2.19 : Synthesis of [1-octyl-3-(3-chloropropyl)-1H-imidazol-3-ium-2-yl]Silver Salt.

2.3.5 Synthesis of [1-octyl-3-(3-chloropropyl)-1H-imidazol-3-ium-2-yl]Silver Salt (3e)

2e (3g) was dissolved in dichloromethane Ag_2O (772mg) were added. The mixture was stirred at room temperature for 48 hours. The optained mixture was filtred and washed with ether. The solvent was evaporated under vacuum and white product was occured. Yield: %76. ^{1}H-NMR (400MHz, $CDCl_3$): δ= 7.45 (s, 1H) 7.03 (s, 1H); 6.89 (s, 1H); 3.90 (t, 2H, J: 6.0 Hz); 1.75 (t, 2H, J: 8.0 Hz); 1.23-1.28 (m, 26H); 0.86 (t, 3H, J: 8.0 Hz) ; FT-IR, (cm^{-1}): 2920, 2848, 1509, 1472, 1227, 1106,1080, 907,816, 664.

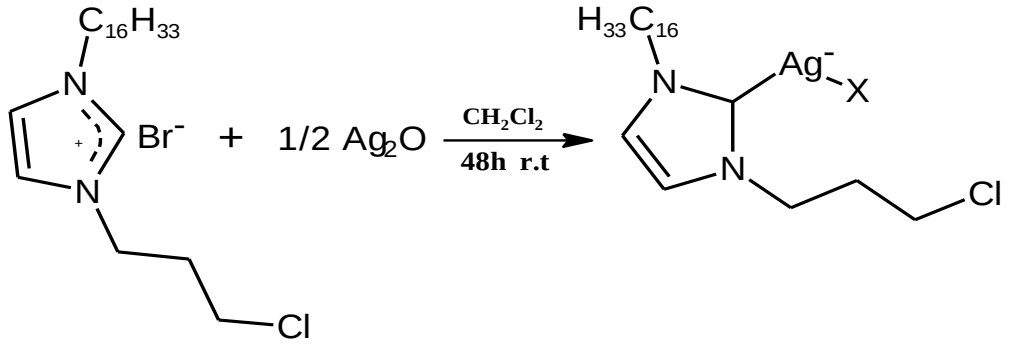


Figure 2.20 : Synthesis of [1-octyl-3-(3-chloropropyl)-1H-imidazol-3-ium-2-yl]Silver Salt.

2.4 Antibacterial Efficacy Tests

It is aimed to develop a woolen fabric which has washing strength in working and exhibits antibacterial activity for a long time. For this purpose, antimicrobial activities of the antimicrobial compounds in the solution environment were first compared and antibacterial efficacy test was carried out according to the international standards in the field of textile on fabric after application of the most effective fabric.

2.4.1 Antibacterial Activity Tests of The Synthesized Compounds

Tests were conducted according to the Mueller-Hinton agar method. Mueller-Hinton agar

metoduna göre testler yapılmıştır [40].

AGAR DILUTION METHOD

The antimicrobial drug is mixed into the agar medium so that each plate contains the drug at different concentrations. Inoculums are simultaneously and rapidly released to the agar surface with instruments (replicators) capable of transferring 32 to 36 inoculums per plague. Here are the general steps for diluting the agar.

1. Materials and Equipment Nutrient: Mueller-Hinton Agar is used.

2. Inoculum Replicators: Most of the inoculum replicators are able to transfer 32 to 36 inoculums per plague. Replicators with a diameter of 3 mm can drop approximately 2 µL (1-3 µL) onto the agar surface. Those with pins smaller than 1 mm can drop about 10 times less, about 0.1-0.2 µL.

3. Preparation of Agar Dilution Plates: The appropriate dilutions of the antimicrobial solutions are added to the molten test agar at 45-50 °C in the water bath. Agar and antimicrobial solution are thoroughly mixed and the mixture is poured into petri dishes on a flat surface, with an agar depth of 3-4 mm.

2.4.1.1 MIC Test According to Mueller Hinton Agar Method of Synthesized Compounds

MIC values were determined by the Mueller Hinton Agar method after the compounds were synthesized and characterized. The common solvent in all compounds was selected as DMSO. 2 type ionic compounds were subjected to the same test, aiming both to determine their likelihood of exhibiting antibacterial activity as well as to ascertain whether or not the Ag-NHC complexes enhance the antibacterial activity.

2.4.2 Antibacterial Efficacy Test Method on Fabric

To quantitatively determine the antibacterial activity, the American Association of Textile Chemists and Colorists (AATCC) 100 method was used. The aim of this method is to quantify the antibacterial rate on textile surfaces. This test system is used to demonstrate bactericidal effects. In the AATCC 100 test method, 1 ml of bacteria is collected from the bacterial concentration prepared with AATCC 6538 gram positive S. aureus bacteria and AATCC 4352 gram negative K.pneumoniae bacteria and sterilized to be absorbed onto two different 48 mm diameter test fabrics to be tested. With a closed container. One of the fabric samples to which the bacteria are impregnated is shaken for 1 minute by adding 100 ml sterile distilled water. Bacterial cultures are passed through the fluid. This sample is called "the sample at time 0". 1 µL of liquid is taken from the sample at time 0 and planted in petri dish. The amount of bacteria obtained is called "the number of bacteria at time 0". If the other bacteria is a sample of fabric impregnated, the oven is removed for 24 hours at 37 °C. At the end of 24 hours, 100 ml of sterile distilled water is added to the fabric sample removed from the oven and shaken for 1 minute. Bacterial cultures are allowed to pass through the liquid. This sample is called the "24 hour sample". 1 micro liter of liquid is taken from the sample at 24 hours and planted in the petri dish. The amount of bacteria obtained is called "the amount of bacteria in 24 hours".

The amount of decrease in bacteria is determined as% value by moving from the number of bacteria at the time of 24 to the number of bacteria at time 0.

$$\%Reduction(CF\,U/ml) = \frac{B - A}{A \times 100}$$

A: The amount of bacteria in "24".

B: Values for the amount of bacteria at time "0".

2.5 Washing Resistance Test of Antibacterial Activity

To determine the resistance to washing of the antibacterial activity, the silver compound coated fabric samples were washed at 50 ^{o}C for 30 minutes each wash time at 60 ^{o}C. using 4 g / l of detergent (CHT COTOBLANC PCS) and the fabrics were dried at 110 ^{o}C in a stiff drier for 4 minutes. Antimicrobial activity assay test was performed for after 5, 10, 20, 30, 40 and 50 washed samples.

2.6 Process of Application

Properties of fabric used in working:

100% wool, interlocking mesh, Nm 40/1, 21 micron fabric.

Fabric Codes:

Raw (control) Fabric: Fabric that is not applied to anything

Untreated: Fabric with silver compound applied but not washed.

2.6.1 Application of Synthesized Compounds to Fabric

There are method of applying the complex to the fabric: this method is binderless method.

The chemical immobilization of the silver compounds to the fabric without using of a binder. For the second method, it is aimed to obtain samples with high washing strength, which can protect the antibacterial property for a long time with the thought that the compounds attached by chemical bonds can not easily be separated from the fabric.

The implementation steps of method is described in detail as follows:

2.6.1.1 Binderless Proceses Prescription

Textile finishing method used: Pulling

Silver Compound-3e: 5 g / lt

Ethanol / water mixture: (1/1) solution was prepared.

According to the shooting method, the process was carried out at 30 ˚C for 1 hour.

Subsequent washes (up to 50 washes) were done at 60 ˚C afterwards. Each of the washes was carried out in a laboratory-type sample dyeing machine for 30 minutes. In the washings, 4 g / l of wash material was used. After the last rinse, final drying was carried out at 4 °C at 110 °C in the braided dryer.

The samples subjected to the application were also done the following tests:

Color measurement

The amount of Ag in ICP-MS

SEM image

Hydrophilicity

Antibacterial efficacy test (according to AATCC 100 method)

2.7 Color Measurement

For the measurement of the color change of the cotton fabrics attached with silver compound in specific quantities, 3 measurements were made for each sample in the Hunterlab Ultrascan Pro computerized color meter and the mean values were taken. Measurements were made with a D65 illuminator and a 10 ° viewing angle. L *, a *, b *, WI (Whiteness index) whiteness index, YI (Yellowness index) yellowness index, C *, h * values are given in the table below.

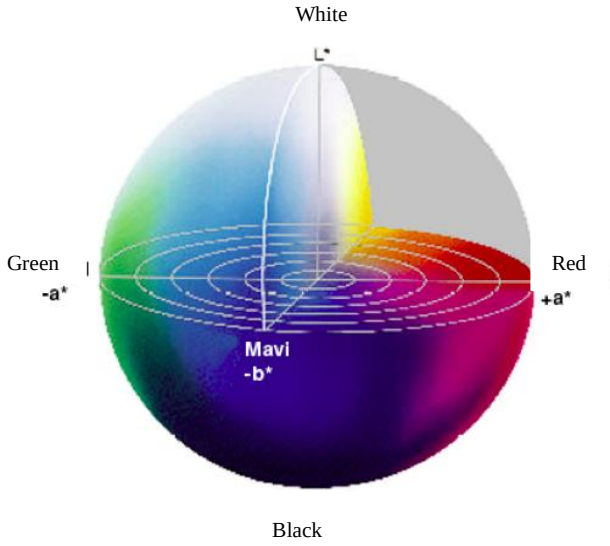


Figure 2.21 : Spatial view of the CIELAB color system.

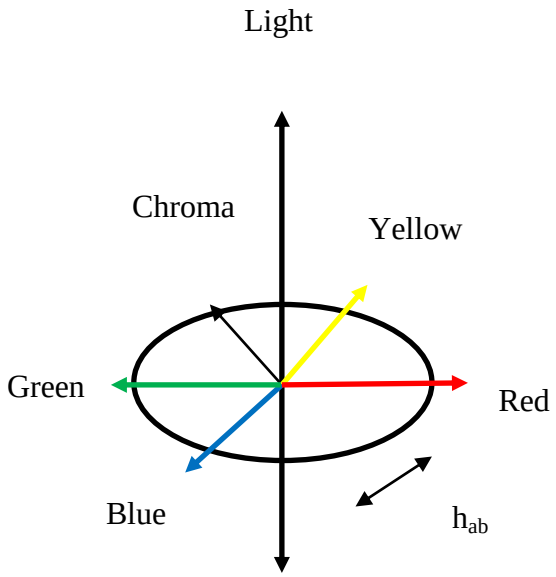


Figure 2.22 : Schematic representatiom of the CIELAB color system.

2.8 Ag analysis with ICP-MS

The amount of Ag in the fabrics was applied to wool fabrics by ICP-MS analysis to quantify the results obtained with biochemical measurements. The important thing here is that all the silver in the fabric can be solved, so 4 different methods have been tried with the experts who make the analysis. The amount of Ag passing through the solution phase was measured by ICP-MS with the repetitive results combustion method.

2.8.1 Acid Degradation Method

6mL HNO_3 + 4mL HCl + 0.5g (max) The fabric sample was placed in Teflon microwave containers. CEM brand microwave oven was brought to 180 ˚C in 15 min and was held at 180˚ C for 15 min. Then, diluted with 50 mL of purified water and ICP-MS analysis was performed.

For acid degradation method, mixtures of acids have been modified, but reproducible and consistent results have not been obtained**.**

2.8.2 ICP-MS Analysis Method According to İncineration Method

Approximately 1g fabric sample was weighed. At 600˚ C, porcelain crucibles were burned (with constant weighing). The flocked fabric samples were also brought to fixed weighing. The burnt samples were combined with 10 mL concentrated HNO_3 and diluted with 50 mL of distilled water. Then, ICP-MS analysis was performed.

During elemental analysis, the flow rate of the plasma gas was set at 15 L / min and the sample depth was set at 7 mm.

2.9 Image of Fabrics with SEM-EDX

Samples are measured at different magnification ratios with using The Carl Zeiss brand EVO LS10 model. Coating with Au was done before measurement.

2.10 Hydrophilicity

Hydrophilicity test measurements are important for showing that the textile material is related to the water.

The silver compound applied fabrics were done the hydrophilicity test according to DIN 53924 standard. Amounts of increase after 90 are measured in mm. The test was repeated 10 times for each fabric sample. The wool fabrics used in the experiments are hydrophilic (water-loving) fabrics. However, the hydrophilicity test was carried out to determine whether the silver compound application had an effect on the hydrophilicity.

3. RESULTS AND DISCUSSIONS

The identity of imidazolium salts and Ag complexes were established by ^{1}H-NMR, ^{13}C-NMR, FT-IR, SEM and ICP-MS.

3.1 Synthesis and Characterization of Imidazol Derivatives

1a, 1b, 1c, 1d and **1e** were synthesized in the presence of 1.5 equiv KOH and 1.1 equiv alkylhalides. Amine function was deprotonated with 1.5 equiv KOH at 50^{o} C for 5h and compound reacted with 1.1 equiv alkylhalide at room temperature for 48 h. **1a** was light yellow oil, **1b** was light orange oil, **1c** was orange oil, **1d** was dark orange oil and **1e** was white solid.

Figure 2.23 : Synthesis of Imidazol Derivatives.

3.1.1 Result of the ^{1}H-NMR, ^{13}C-NMR and FTIR for 1a

In ^{1}H-NMR spectrum (Appendıces 1) of 1a has s.ignals at 6.89; 7.01; 7.45 ppm for protons of imidazole, at 3.95 ppm for CH_2 protons and at 1.42 ppm for CH_3 protons. In ^{13}C-NMR spectrum are shown in article [93]. Analysis of FT-IR spectroscopy also has shown us coordination of ethyl with N atom, by the disapperance of the NH vibrations at 3200 cm^{-1}. FT-IR spectrum of 1a (Appendıces 2) has a vibration at 1300-1000 cm^{-1} (NC), at 2900-2800 cm^{-1} aliphatic (CH) were observed.

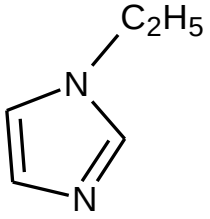


Figure 2.24 : 1-Ethyl-*1H*-imidazole.

3.1.2 Result of the ^{1}H-NMR, ^{13}C-NMR and FT-IR for 1b

In ^{1}H-NMR spectrum (Appendıce 3) of 1b has signals at 6.89-7.45 ppm for protons of imidazole, at 1.24-3.88 ppm for CH_2 protons and at 0.90 ppm for CH_3 protons. In ^{13}C-NMR spectrum are shown in article [93]. Analysis of FT-IR spectroscopy also has shown us coordination of buthyl with N atom, by the disapperance of the NH vibrations at 3200 cm-1. FT-IR spectrum of 1b (Appendıce 4) has a vibration at 1300-1000 cm^{-1} (NC), at 2900-2800cm^{-1} aliphatic (CH) were observed.

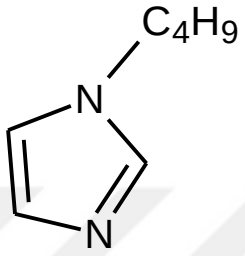


Figure 2.25 : 1-Buthyl-*1H*-imidazole.

3.1.3 Result of the ^{1}H-NMR, ^{13}C-NMR and FT-IR for 1c

In ^{1}H-NMR spectrum (Appendıce 5) of 1c has signals at 6.86-7.42 ppm for protons of imidazole, at 1.23-3.88 ppm for CH_2 protons and at 0.84 ppm for CH_3 protons. In ^{13}C-NMR spectrum are shown in article [94]. Analysis of FT-IR spectroscopy also has shown us coordination of octhyl with N atom, by the disapperance of the NH vibrations at 3200 cm^{-1} . FT-IR spectrum of 1c (Appendıce 6) has a vibration at 1300-1000 cm^{-1} (NC), at 2900-2800cm^{-1} aliphatic (CH) were observed.

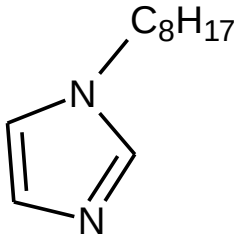


Figure 2.26 : 1-octyl-1H-imidazole.

3.1.4 Result of the ^{1}H-NMR, ^{13}C-NMR and FT-IR for 1d

In ^{1}H-NMR spectrum (Appendıce 7) of 1d has signals at 6.87-7.43 ppm for protons of imidazole, at 1.24-3.89 ppm for CH_2 protons and at 0.86 ppm for CH_3 protons. In ^{13}C-NMR spectrum are shown in article [94]. Analysis of FT-IR spectroscopy also has shown us coordination of dodechyl with N atom, by the disapperance of the NH vibrations at 3200 cm^{-1}. FT-IR spectrum of 1d (Appendıce 8) has a vibration at 1300-1000cm^{-1} (NC), at 2900-2800 cm^{-1} aliphatic (CH) were observed.

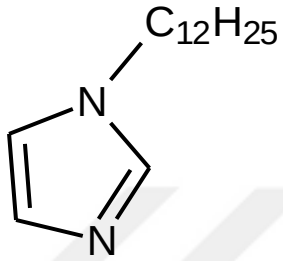


Figure 2.27 : 1-dodecyl-1H-imidazole.

3.1.5 Result of the ^{1}H-NMR, ^{13}C-NMR and FT-IR for 1e

In 1H-NMR spectrum (Appendıce 9) of 1e has signals at 6.87-7.43 ppm for protons of imidazole, at 1.24-3.89 ppm for CH_2 protons and at 0.86 ppm for CH_3 protons. In 13C-NMR spectrum are shown in article [94]. Analysis of FT-IR spectroscopy also has shown us coordination of hexadecyl with N atom, by the disapperance of the NH vibrations at 3200cm-1 FTIR spectrum of 1e (Appendıce 10) has a vibration at 1300-1000 cm-1 (NC), at 2900-2800 cm-1 aliphatic (CH) were observed.

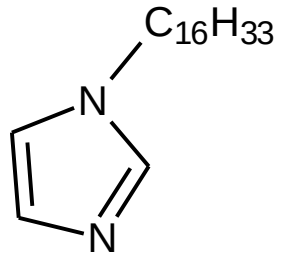
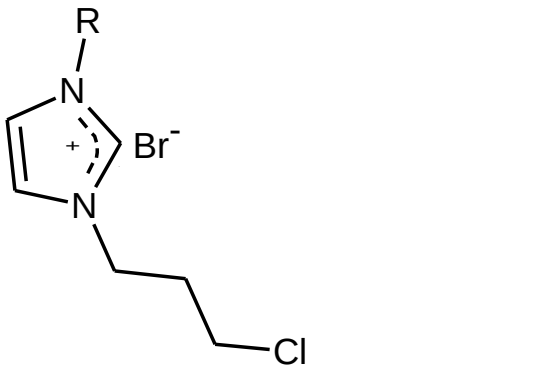


Figure 2.28 : 1-hexadecyl-1H-imidazole.

3.2 Synthesis and Characterization of Imidazolium salts

2a, 2b,2c,2d and **2e** were synthesized in the presence of 1.1 equiv 1-Bromo-3-choloropropane. Amine function was reacted with 1.1 equiv 1-Bromo-3-

choloropropane at 110˚ C for 24 h (Figure 3.7). **2a** was yellow oil, **2b** and **2c** were brown oil, **2d** was orange oil and **2e** was white solid.



R: ethyl, buthyl, octyl, dodecyl, hexadec

Figure 2.29 : Synthesis of Imidazolium Salts.

3.2.1 Result of the ^{1}H-NMR, ^{13}C-NMR and FT-IR for 2a

In ^{1}H-NMR spectrum (Appendıce 11) of 2a has signals at 9.74 ppm for protons of imidazole (NCHN), at 7.93-7.69 ppm for (CH = CH), at 4.63 ppm for ($N(CH_2)_3$) protons, at 2.05 ppm (NCH_2) protons and at 1.69 ppm for CH_3 protons. Analysis of FT-IR spectroscopy also has shown us coordination of butyl with N atom, by the disapperance of the NH vibrations at 3400-3200. FT-IR spectrum of 2a (Appendıce 12) has a vibration at 3000-2800 cm^{-1} aliphatic

(CH), 1800-1500 cm^{-1} (N = C), at 1300-1000cm^{-1} (NC), at 800-600 cm^{-1} aromatic ring were observed.

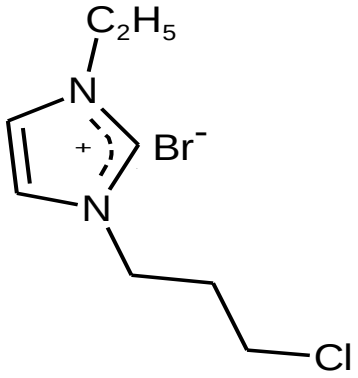


Figure 2.30 : [1-ethyl-3-(3-chloropropyl)imidazolium bromide] (2a).

3.2.2 Result of the ^{1}H-NMR, ^{13}C-NMR and FT-IR for 2b

In ^{1}H-NMR spectrum (Appendıce 13) of 2b has signals at 10.09 ppm for protons of imidazole(NCHN), at 8.16-7.37 ppm for (CH = CH), at 4.63-2.27 ppm for

($N(CH_2)_3$) protons, at 1.83-1.30 ppm(NCH_2) protons and at 0.87 ppm for $–CH_3$ protons. In ^{13}C-NMR spectrum (Appendıce 14) of 2b has signals 136.6;123.8;121.5 ppm for carbon of imidazole , at 50.5; 46.3; 29.5 ppm for ($N(CH_2)_3Cl$) carbons, at 29.3; 26.0; 22.6; 14.5 ppm for ($N(CH_2)_4$) carbons. Analysis of FT-IR spectroscopy also has shown us coordination of butyl with N atom, by the disapperance of the N-H vibrations at 3400-3200. FT-IR spectrum of 2b (Appendıce 15) has a vibration at 3000-2800 cm^{-1} (aliphatic (CH), 1800-1500 cm^{-1} (N = C), at 1300-1000cm^{-1} (NC), at 800-600 cm^{-1} aromatic ring were observed.

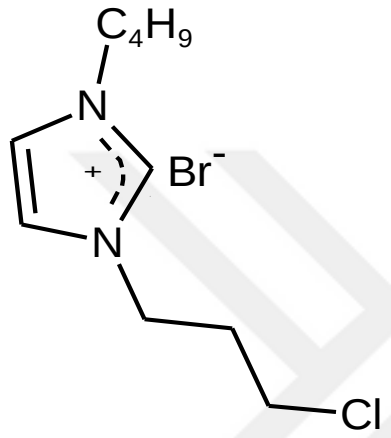


Figure 2.31 : [1-butyl-3-(3-chloroproyl)imidazolium bromide] (2b).

3.2.3 Result of the ^{1}H-NMR, ^{13}C-NMR and FT-IR for 2c

In ^{1}H-NMR spectrum (Appendıce 16) of 2c has signals at 9.40 ppm for protons of imidazole (NCHN), at 7.84-7.66 ppm for (CH = CH), at 4.25-2.41 ppm for ($N(CH_2)_3$) protons, at 1.77-1.22 ppm(NCH_2) protons and at 0.82 ppm for $–CH_3$ protons. In ^{13}C-NMR spectrum (Appendıce 17) of 2c has signals 142.5, 125.1, 123.6, ppm for carbon of imidazole , at 50.2, 46.3, 29.5, ppm for ($N(CH_2)_3Cl$) carbons, at 29.3; 26.0; 22.6; 14.5 ppm for ($N(CH_2)_8$) carbons. Analysis of FT-IR spectroscopy also has shown us coordination of butyl with N atom, by the disapperance of the N-H vibrations at 3400-3200. FT-IR spectrum of 2c (Appendıce 18) has a vibration at 3000-2800 cm^{-1} aliphatic (CH), 1800-1500 cm^{-1} (N = C), at 1300-1000 cm^{-1} (NC), at 800-600 cm^{-1} aromatic ring were observed.

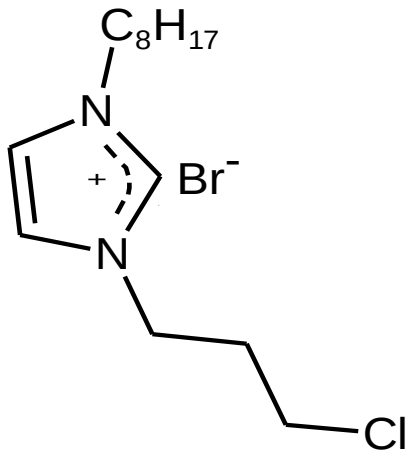


Figure 2.32 : [1-octyl-3-(3-chloropropyl)imidazolium bromide] (2c).

3.2.4 Result of the ^{1}H-NMR, ^{13}C-NMR and FT-IR for 2d

In ^{1}H-NMR spectrum (Appendıce 19) of 2d has signals at 10.19 ppm for protons of imidazole(NCHN), at 8.82-7.26 ppm for (CH = CH), at 4.68-1.86 ppm for ($N(CH_2)_3$) protons, at 1.20-1.28 ppm(NCH_2) protons and at 0.82 ppm for $–CH_3$ protons. In ^{13}C-NMR spectrum (Appendıce 20) of 2c has signals 136.4, 123.8, 121.6, ppm for carbon of imidazole , at 50.2, 46.7, 31.9, ppm for ($N(CH_2)_3Cl$) carbons, at 31.1, 30.1, 29.6, 29.5, 29.4, 29.3, 29.0, 26.3, 22.6, 14.1 ppm for (N $(CH_2)_{12}$) carbons. Analysis of FT-IR spectroscopy also has shown us coordination of butyl with N atom, by the disapperance of the N-H vibrations at 3400-3200. FT-IR spectrum of 2d (Appendıce 21) has a vibration at 3000-2800 cm^{-1} aliphatic (CH), 1800-1500 cm^{-1} (N = C), at 1300-1000cm^{-1} (NC), at 800-600 cm^{-1} aromatic ring were observed.

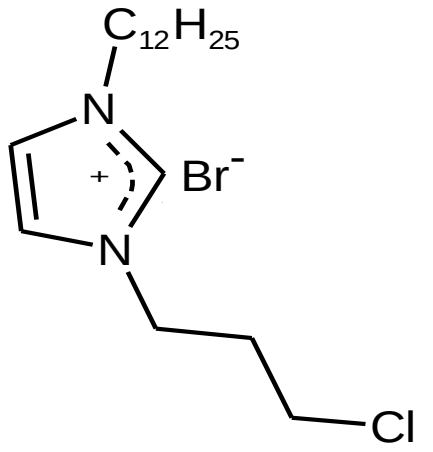


Figure 2.33 : [1-dodecly-3-(3-chloropropyl)imidazolium bromide] (2d).

3.2.5 Result of the ^{1}H-NMR, ^{13}C-NMR and FT-IR for 2e

In ^{1}H-NMR spectrum (Appendıce 22) of 2e has signals at 10.19 ppm for protons of imidazole(NCHN), at 8.8-7.23 ppm for (CH = CH), at 4.70-2.85 ppm for ($N(CH_2)_3$) protons, at 1.88-1.22 ppm(NCH_2) protons and at 0.85 ppm for $-CH_3$ protons. In ^{13}C-NMR spectrum (Appendıce 23) of 2e has signals 136.4, 123.8, 121.5, ppm for carbon of imidazole , at 50.2, 46.7, 30.1, ppm for ($N(CH_2)_3Cl$) carbons, at29.7, 29.6, 29.6, 29.6, 29.5, 29.4, 29.3, 29.0, 26.3, 22.6, 14.1 ppm for ($N(CH_2)_{12}$) carbons. Analysis of FT-IR spectroscopy also has shown us coordination of butyl with N atom, by the disapperance of the N-H vibrations at 3400-3200. FT-IR spectrum of **2e** (Appendıce 24) has a vibration at 3000-2800 cm^{-1} aliphatic (CH), 1800-1500 cm^{-1} (N = C), at 1300-1000cm^{-1} (NC), at 800-600 cm^{-1} aromatic ring were observed.

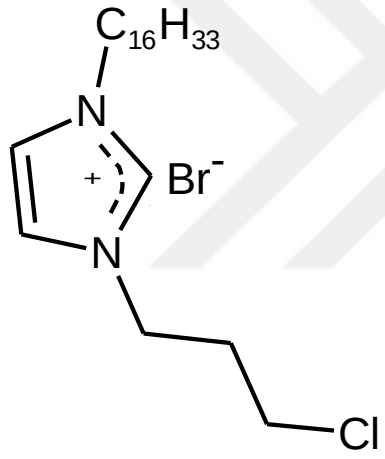
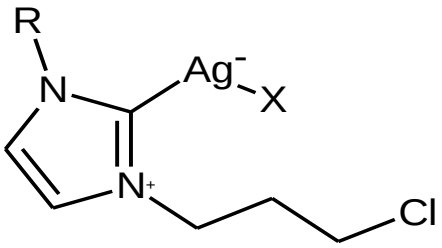


Figure 2.34 : [1-hexadecyl-3-(3-kloropropyl)imidazolium bromide] (2e)

3.3 Synthesis and Characterization of Silver Complexes

3a, 3b, 3c, 3d and **3e** were synthesized in the presence of ½ equiv silver oxide. Compound reacted with ½ equiv silver oxide at room temperature for 48 h. **(Figure 3.13) 3a** was white solid, **3b** was brown solid, **3c** was grey solid, **3d** was dark. Brown solid and **3e** was white solid.



R: ethyl, buthyl, octyl, dodecyl, hexadec

X: Br, I

Figure 2.35 : Synthesis of Silver Complexes.

3.3.1 Result of the ^{1}H-NMR, ^{13}C-NMR and FT-IR for 3a

In ^{1}H-NMR spectrum (Appendıce 25) of 3a has signals at 7.76-7.52 ppm for protons of imidazole, at 4.06-2.48 ppm CH_2Cl, at 1.42 ppm for CH_2 protons and at 1.33 ppm for CH_3 protons. Analysis of FT-IR spectroscopy also has shown us coordination of ethyl with N atom, by the disapperance of the NH vibrations at 3400-3200, FT-IR spectrum of 3a (Appendıce 26) has a vibration at 3000-2800 cm^{-1} aliphatic (CH), at 18000-1500 cm^{-1} (N = C), at 1300-1000 cm^{-1} (NC), at 800-600 cm^{-1} aromatic ring, at 600 < cm^{-1} CCl were observed.

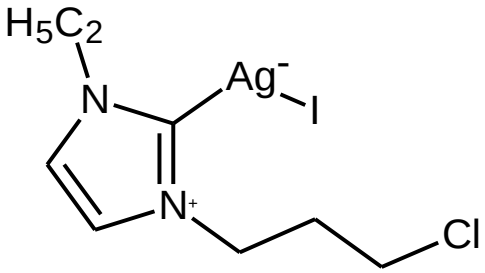


Figure 2.36 : [1-Ethyl-3-(3-chloropropyl)-1H-imidazol-3-ium-2-yl]silver (3a).

3.3.2 Result of the ^{1}H-NMR, ^{13}C-NMR and FT-IR for 3b

In ^{1}H-NMR spectrum (Appendıce 27) of 3b has signals at 7.44-7.05 ppm for protons of imidazole, at 4.-2.511 ppm for $(CH_2)_3Cl$ protons, at 1.78-1.22 ppm for CH_2 protons and at 0.85 ppm for CH_3 protons. In ^{13}C-NMR spectrum (Appendıce 28) of 3b has signals 123.1, 121.5, 120.5, ppm for carbon of imidazole , at 51.59, 47.55, 42.70, ppm for $(N(CH_2)_3Cl)$ carbons, at 38.76, 34.51, 32.85, 19.08, 13.57 ppm for ($N(CH_2)_{12}$) carbons. Analysis of FT-IR spectroscopy also has shown us coordination of ethyl with N atom, by the disapperance of the NH vibrations at 3400-3200, FT-IR

spectrum of 3b (Appendıce 29) has a vibration at 3000-2800 cm^{-1} aliphatic (CH), at 18000-1500 cm^{-1} (N = C), at 1300-1000 cm^{-1} (NC), at 800-600 cm^{-1} aromatic ring, at 600 < cm^{-1} CCl were observed.

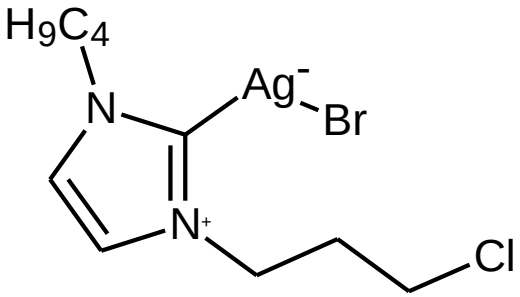


Figure 2.37 : [1-Butyl-3-(3-chloropropyl)-1H-imidazol-3-ium-2-yl]silver (3b).

3.3.3 Result of the ^{1}H-NMR, ^{13}C-NMR and FT-IR for 3c

In ^{1}H-NMR spectrum (F Appendıce 30) of **3c** has signals at 8.18-7.21 ppm for protons of imidazole, at 4.26-4.08 ppm for $(CH_2)_3Cl$ protons, at 1.89-1.21ppm for CH_2 protons and at 0.86 ppm for CH_3 protons. Analysis of FT-IR spectroscopy also has shown us coordination of ethyl with N atom, by the disapperance of the NH vibrations at 3400-3200. FT-IR spectrum of 3b (Appendıce 31) has a vibration at 3000-2800 cm^{-1} aliphatic (CH), at 18000-1500 cm^{-1} (N = C), at 1300-1000 cm^{-1} (NC), at 800-600 cm^{-1} aromatic ring, at 600 < cm^{-1} CCl were observed.

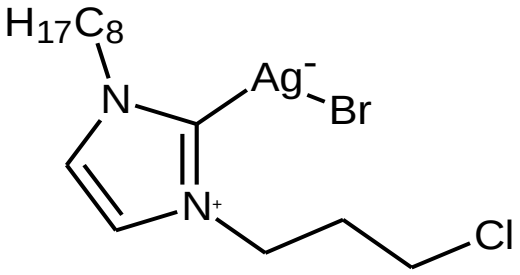


Figure 2.38 : [1-Octyl-3-(3-chloropropyl)-1H-imidazol-3-ium-2-yl]silver (3c).

3.3.4 Result of the ^{1}H-NMR, ^{13}C-NMR and FT-IR for 3d

In ^{1}H-NMR spectrum (Appendıce 32) of 3d has signals at 8.18-7.21 ppm for protons of imidazole, at 4.26-4.08 ppm for $(CH_2)_3Cl$ protons, at 1.89-1.21ppm for CH_2 protons and at 0.86 ppm for CH_3 protons. In ^{13}C-NMR spectrum (Appendıce 33) of 3d has signals 123.0, 121.3, 120.7, 121.5, ppm for carbon of imidazole , at 78.53, 75.48, 32.76, ppm for $(N(CH_2)_3Cl)$ carbons, at 29.28, 29.02, 26.86, 21.25, 13.47 ppm

for ($N(CH_2)_{12}$) carbons. Analysis of FT-IR spectroscopy also has shown us coordination of ethyl with N atom, by the disapperance of the NH vibrations at 3400-3200. FT-IR spectrum of 3d (Appendce 34) has a vibration at 3000-2800 cm^{-1} aliphatic (CH), at 18000-1500 cm^{-1} (N = C), at 1300-1000 cm^{-1} (NC), AT 800-600 cm^{-1} aromatic ring, at 600 < cm^{-1} CCl were observed.

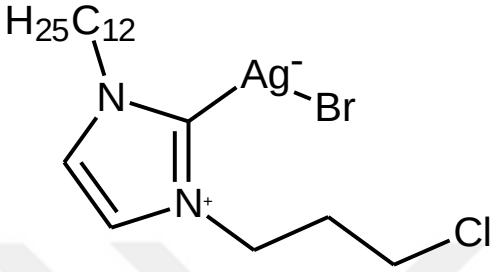


Figure 2.39 : [1-Dodecyl-3-(3-chloropropyl)-1H-imidazol-3-ium-2-yl]silver (3d).

3.3.5 Result of the ^{1}H-NMR, ^{13}C-NMR and FT-IR for 3e

In ^{1}H-NMR spectrum (Appendıce 35) of 3e has signals at 7.45-6.89 ppm for protons of imidazole, at 3.90-1.75 ppm for $(CH_2)Cl$ protons, at 1.23-1.28 ppm for CH_2 protons and at 0.86 ppm for CH_3 protons. Analysis of FT-IR spectroscopy also has shown us coordination of ethyl with N atom, by the disapperance of the NH vibrations at 3400-3200. FT-IR spectrum of 3e (Appendıce 36) has a vibration at 3000-2800 cm^{-1} aliphatic (CH), at 18000-1500 cm^{-1} (N = C), at 1300-1000 cm^{-1} (NC), AT 800-600 cm^{-1} aromatic ring, at 600 < cm^{-1} CCl were observed.

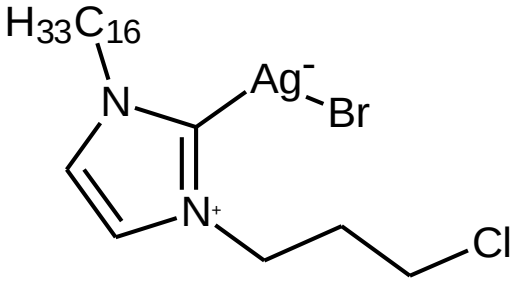


Figure 2.40 : [1-Hexadecyl-3-(3-chloropropyl)-1H-imidazol-3-ium-2-yl]silver (3e).

3.4 The Results Of The MIC Assay According to The Mueller Hinton Agar Method of The Synthesized Compounds

The MIC values of the synthesized compounds are given in Table 3.1.

Table 3.1 : The MIC Values of the Synthesized Compounds.

Molecues	S. Aureus	E. Faecalis	E. Coli	P. Aeruginosa	C. Albicans	C. Tropicalis
2a	400	400	800	800	400	400
2b	200	200	800	800	200	100
2c	12.5	12.5	50	50	25	25
2d	12.5	12.5	50	50	12.5	12.5
2e	200	200	200	200	100	100
3a	200	200	400	400	200	200
3b	100	50	200	200	50	50
3c	200	100	400	400	100	100
3d	6.25	6.25	12.5	12.5	6.25	6.25
3e	50	50	200	50	50	50
CONTROL1	There is growing.	There is growing.	There is growing.	There is growing.	There is growing.	There is growing.
CONTROL2	There is growing.	There is growing.	There is growing.	There is growing.	There is growing.	There is growing.

3.5 Results of Antibacterial Efficacy Test

The antibacterial activity of the synthesized compounds was first tested in soluble form according to the Müller-Hinton Agar test. In these experiments, compounds with Cl groups in the structure for wool fabric were preferred from the compounds that gave the best results. When the antibacterial activity test of the synthesized compounds was tested against gram positive, gram negative and fungi, a gram positive test determined on the textile reference test method (AATCC 100) was tested against S.Aureus (gram negative) and K.pnem (gram positive) bacteria.

3.6 Mechanism of Antibacterial Effect and Immobilizatio to Fabric of The Complex

Explaination of antibacterial mechanism for silver: The silver complex damages the protein groups in the cell membrane. It binds to the thiol groups and enters the cell. Bacteria penetrates. Then silver ions release of the intracellular. Thus, it increases bactericidal activity and inhibits the respiratory chain. Antimicroabial agent does not direct contact with bacteria.

$H_2O + {}^1/_2\, O_2 \xrightarrow{Metal\ ion} H_2O_2 \rightarrow H_2O + (O)$. Because this mechanism with produced active oxygen diffuses from wool fabric to the surrounding.

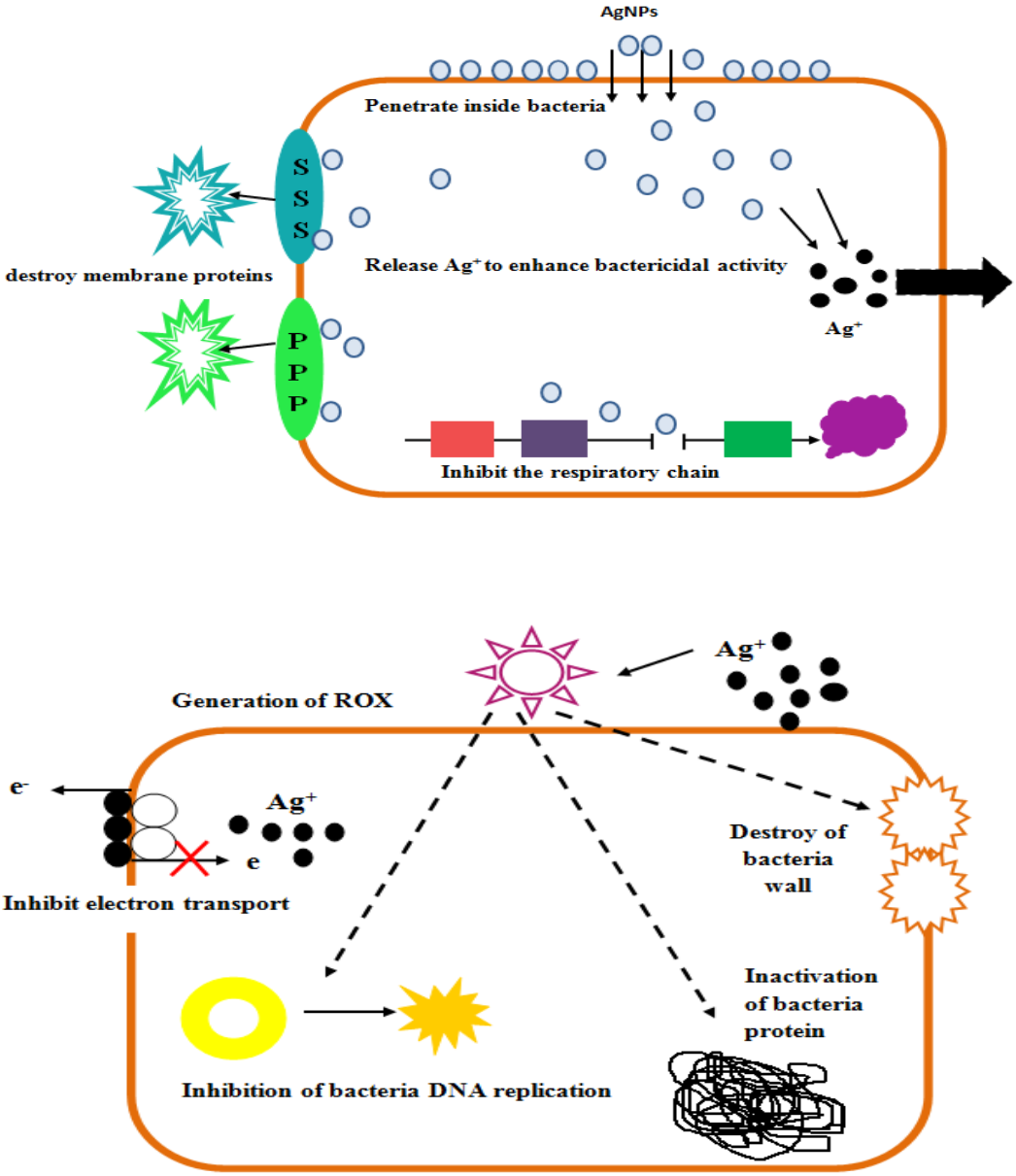


Figure 2.41 : Antibacterial mechanism for silver[50].

The amino groups of the wool fabric interact with the chlorine groups in the silver complex that is synthesized. The chemical reaction occurs. A new bond is formed between the N in the wool structure and the carbon attached to Cl in the complex. In this way, the complex fabric is chemically bonded.

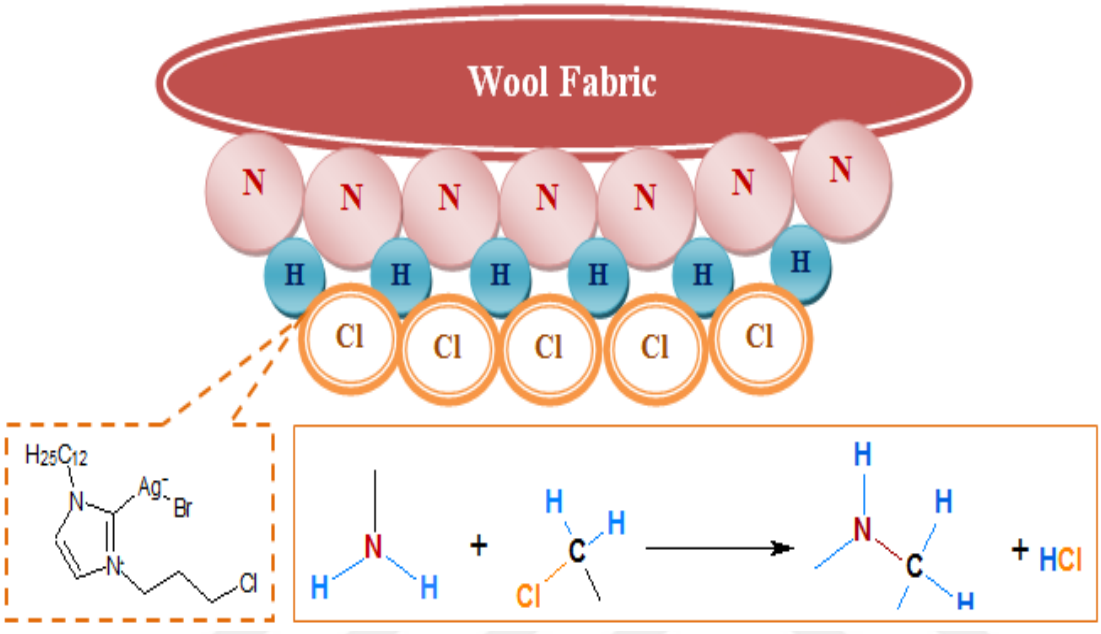


Figure 2.42 : Chemical bonding.

3.7 The AATCC Test Results of the Fabrics Entrained in The Silver Complex

Wool fabric holding experiment was made according to the shooting method and antibacterial efficiency test results are given in Table 3.2. Wool fabric holding experiment was made according to the İmpregnation method with 3d compound and antibacterial efficiency test results are given in Table 3.3.

Two silver complexs have been tried to optimize application condition to wool fabrics with the changing temperature (30˚ C, 45˚ C, 60˚ C, 90˚ C) and time (1 hour, 3 hour). As an aplication condition 30˚ C and 1 h was decided as result of perfect antibacterial test results without time and temperature variation. Matting of wool in temperate conditions was the reason of preference. But, super washed wool fabric was decided against to probability of worse antibacterial result in tempere condition. In this manner, optimum application conditions and parameters were clarified. Only these conditions have been used for futher test.

Table 3.2 : Antibacterial Activity Results of Wool Fabrics Applied Silver Compound at Different Times and Temperatures According to the Shooting Method.

Wash Number	0. Hour		24.Hour			
	S. AUREUS	K. PNEUMONİAE	S.AUREUS		K.PNEUMONİAE	
			lıve bacterıum number	% bacterıa reductıon	lıve bacterıum number	**% bacterıa reductıon**
Raw wool fabric	156000	1510000	130000	% 16.67	215000	**% 20.47**
3d, 30˚ C, 1hour	340000	250000	25	99.99	40	**99.98**
3d, 30˚ C, 3hour	340000	250000	56	99.98	22	**99.99**
3d, 45˚ C, 1hour	340000	250000	100	99.97	15	**99.99**
3d, 60˚ C, 1hour	340000	250000	32	99.99	16	**99.99**
3d, 90˚ C, 1hour	**340000**	**250000**	**44**	**99.99**	**19**	**99.99**

According to the table, it can be seen that the wool fabric applied with the silver compound (3d) according to the impregnation method shows 99.93 % antibacterial activity against gram-positive S. aureus and 99.63 % against gram-negative K.pneumoniae. The efficacy after 5 washes decreased to 99.17 % against gram-positive S. aureus and 99.40% against gram-negative K.pneumoniae. At the end of 30 washes the efficacy decreased to 97.74% against gram-positive S. aureus and to 66.55 % against gram-negative K.pneumoniae. At the end of 50 washes, the activity decreased to 97.65 % against gram-positive S. aureus and to 65.17 % against gram-negative K. pneumoniae. From here it appears that your silver compound is more effective against gram-positive S. aureus.

Table 3.3 : Antibacterial Activity of Silver Compound Applicated Wool Fabrics According to Impregnation Method and Results of Washing Strength of Antibacterial Efficacy After 50 Washes (3d).

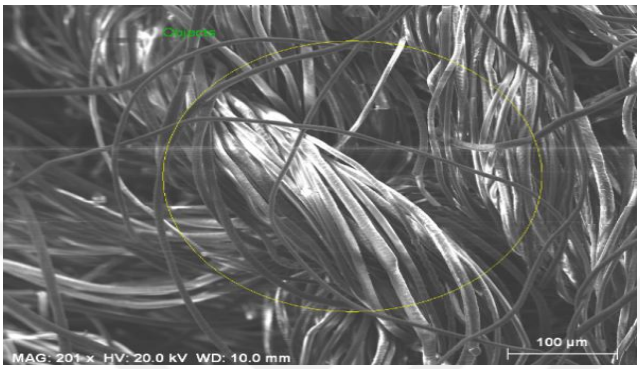
wash number	0. hour		24.hour			
			S.Aureus		**K.Pneumoniae**	
	s. aureus	k. pneumoniae	lıve bacterıum number	% bacterıa reductıon	lıve bacterıum number	**% bacterıa reductıon**
Without binder unprocessed	310000	290000	220	99.93	1080	**99.63**
Without binder 5th washing	310000	290000	2580	99.17	1750	**99.40**
Without binder 10th washing	310000	290000	3010	99.03	2500	**99.14**
Without binder 20th washing	310000	290000	4360	98.59	5600	**98.07**
Without binder 30.th washing	310000	290000	7000	97.74	97000	**66.55**
Without binder 40th washing	310000	290000	7200	97.68	99500	**65.69**
Without binder 50th washing	**310000**	**290000**	**7300**	**97.65**	**101000**	**65.17**

3.8 Fabric Pendency Data

Complexes containing Cl groups that easily react chemically with the NH_2 groups in the natural structure of the yam have been preferred in wool fabric processing. Post-pendency test and analysis were done for 3e complex.

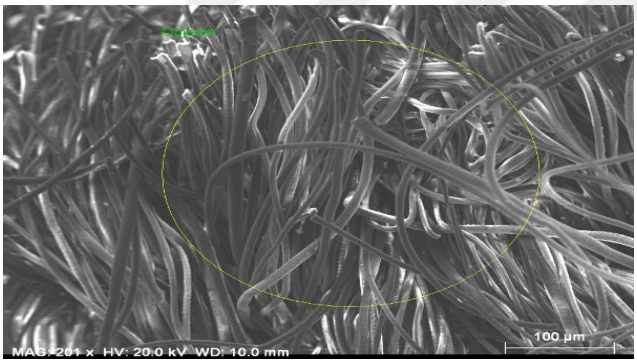
3.9 Result of SEM-EDX Analysis

The silver comlex (3d) which is wanted to be developed textile finishing process, was tried to be retained by applying the pulling method. SEM-EDX images and analysis results of wool fabrics obtained with these 3e complexes are given in Figure 3.1.



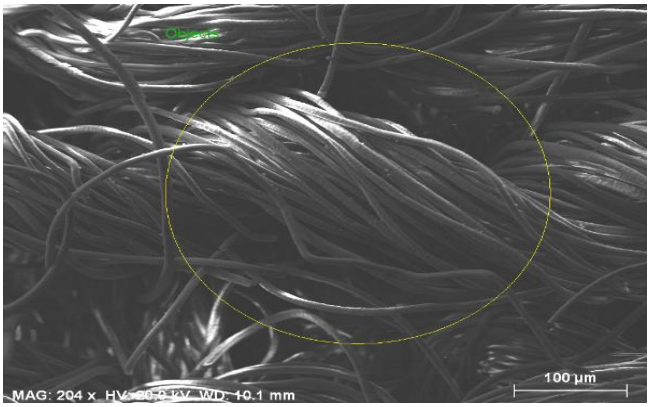
Element	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error [%]
Carbon	K-series	44.29	44.29	48.27	13.8
Nitrogen	K-series	55.29	55.29	51.68	18.5
Silver	L-series	0.42	0.42	0.05	0.

Raw Wool

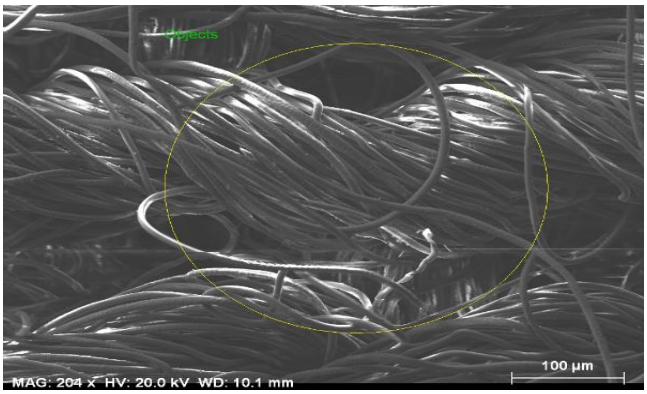


Element	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error [%]
Carbon	K-series	45.41	45.41	49.43	14.4
Nitrogen	K-series	54.12	54.12	50.52	19.0
Silver	L-series	0.47	0.47	0.06	0.0

Unprocessed

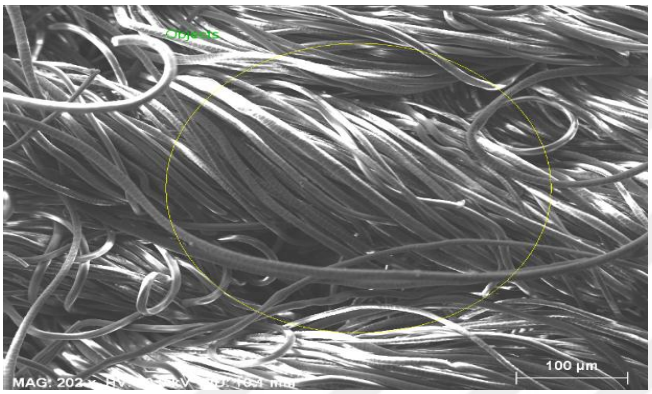


Element	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error [%]
Carbon	K-series	44.96	44.96	49.01	14.1
Nitrogen	K-series	54.46	54.46	50.92	18.7
Silver	L-series	0.58	0.58	0.07	0.0

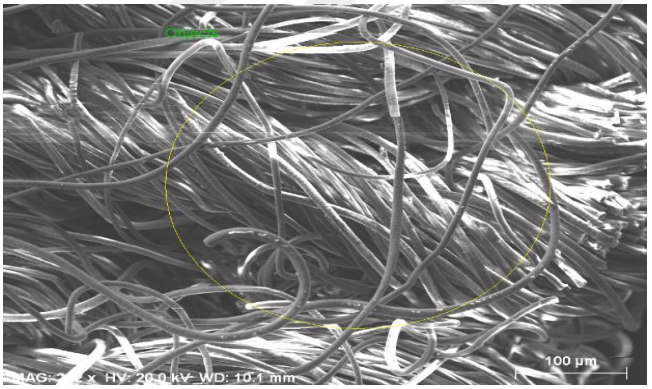


Element	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error [%]
Carbon	K-series	45.41	45.41	49.40	14.5
Silver	L-series	0.41	0.41	0.05	0.0
Nitrogen	K-series	54.18	54.18	50.55	19.4

5 Wash

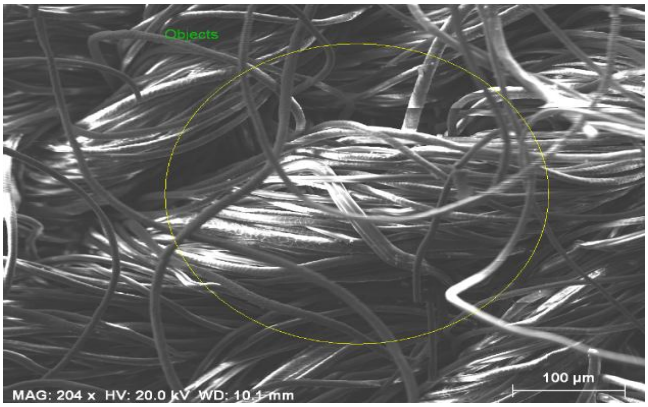


Element	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error [%]
Carbon	K-series	43.53	43.53	47.48	13.8
Nitrogen	K-series	56.11	56.11	52.48	19.6
Silver	L-series	0.36	0.36	0.04	0.0

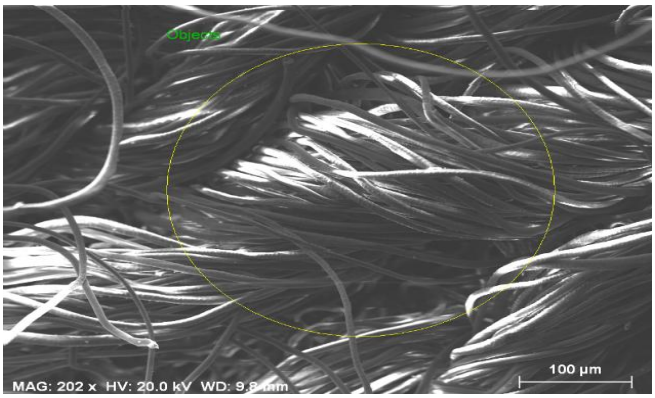


Element	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error [%]
Carbon	K-series	46.73	46.73	50.68	14.8
Nitrogen	K-series	53.00	53.01	49.29	19.0
Silver	L-series	0.26	0.26	0.03	0.0

10 Wash

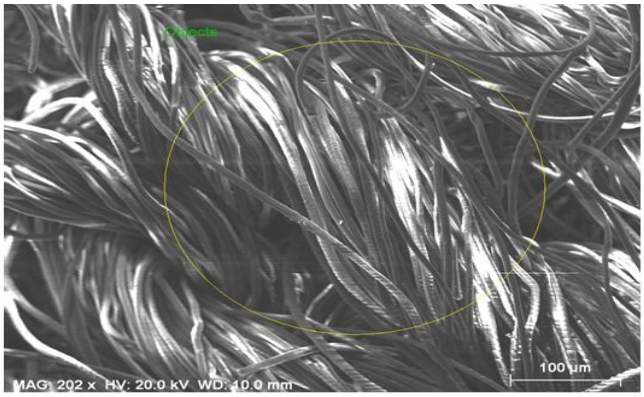


Element	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error [%]
Carbon	K-series	44.35	44.35	48.40	13.8
Silver	L-series	0.57	0.57	0.07	0.0
Nitrogen	K-series	55.08	55.08	51.53	18.5

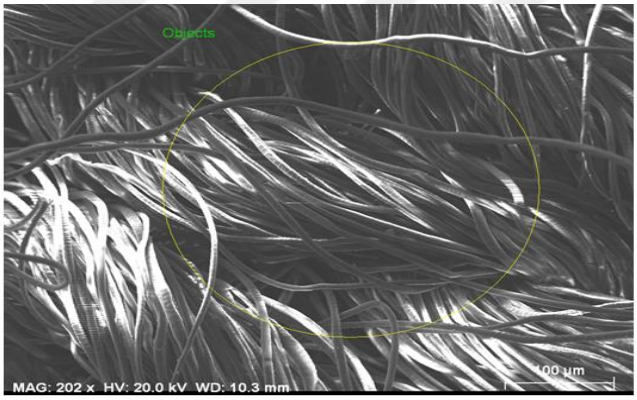


Element	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error [%]
Carbon	K-series	43.07	43.07	47.01	13.6
Nitrogen	K-series	56.56	56.57	52.94	19.6
Silver	L-series	0.36	0.36	0.04	0.0

20 Wash

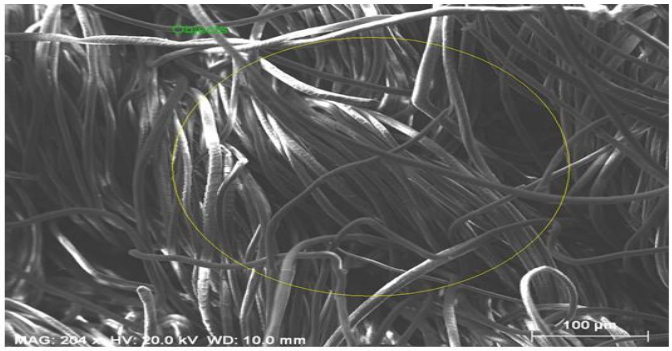


Element	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error [%]
Carbon	K-series	45.29	45.29	49.29	14.1
Silver	L-series	0.42	0.42	0.05	0.0
Nitrogen	K-series	54.28	54.28	50.66	18.4

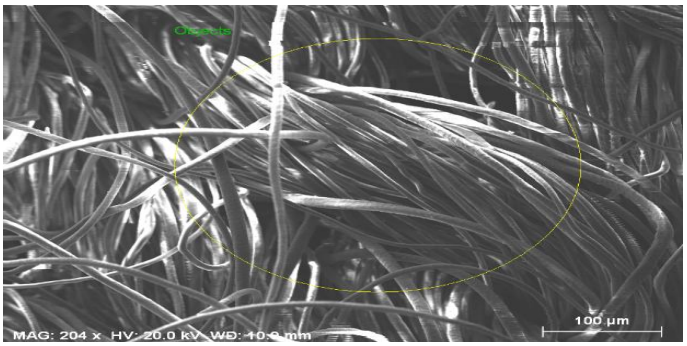


Element	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error [%]
Carbon	K-series	44.87	44.87	48.79	14.2
Nitrogen	K-series	54.87	54.88	51.17	19.1
Silver	L-series	0.26	0.26	0.03	0.0

30 Wash

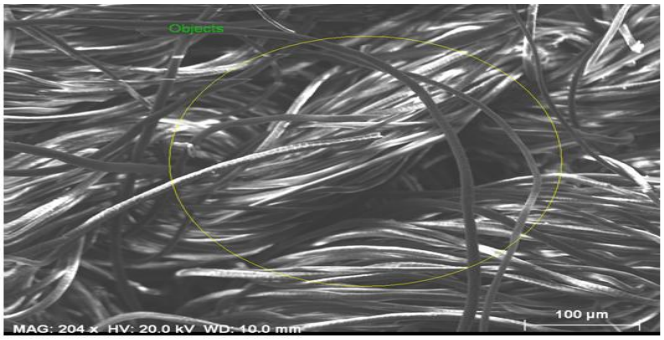


Element	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error [%]
Carbon	K-series	42.48	42.48	46.47	13.6
Nitrogen	K-series	57.01	57.01	53.47	20.2
Silver	L-series	0.51	0.51	0.06	0.0

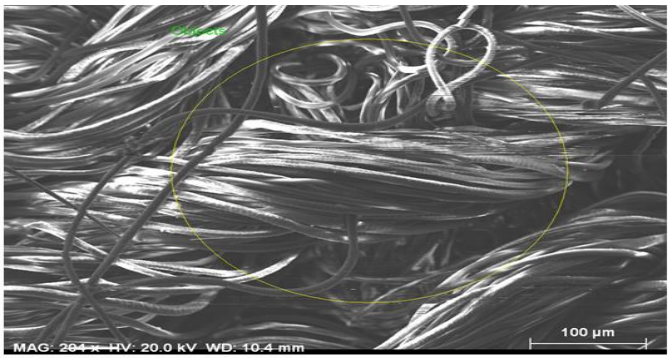


Element	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error [%]
Carbon	K-series	43.74	43.74	47.68	14.0
Nitrogen	K-series	55.93	55.93	52.28	20.2
Silver	L-series	0.32	0.32	0.04	0.0

40 Wash



Element	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error [%]
Silver	L-series	0.54	0.54	0.07	0.0
Nitrogen	K-series	55.67	55.67	52.13	18.9
Carbon	K-series	43.78	43.78	47.81	13.7



Element	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error [%]
Silver	L-series	0.29	0.29	0.04	0.0
Carbon	K-series	47.65	47.65	51.62	14.7
Nitrogen	K-series	52.05	52.05	48.35	17.1

50 Wash

Figure 2.43 : SEM-EDX Images and Analysis Results of Wool Fabrics Obtained with 3d Complexes.

A homogeneous distribution is not observed in wool fabrics impregnated with 3d complex. In the randomly selected areas, the Ag amount is in the range of 0.26-0.58 % by weight. This shows us that the complex is impregnated on the fabric and that the impregnate rate is roughly applicable to the field of medical textiles. ICP-MS data are based on this issue. The treatment conditions for 1 hour at 30° C were sufficient for the complex to be impregnated on the wool fabric. The values measured here are also parallel with antibacterial efficacy tests.

3.10 Results of the ICP-MS

ICP-MS results show that amount of silver reduced with wash on the wool rabric. After 30th wash silver ions significantly reduced on fabric. This station is harmony with antibacterial efficacy test results.

Table 3.4 : The amount of Ag found before and after washing on wool fabric with shooting method (3d).

Fabrics	Ag Amount (mg/g)
Without binder Unprocessed	135
5th washing without binders	89
10th washing without binders	84
20th washing without binders	88
30th washing without binders	74
40th washing without binders	6.271
50th washing without binders	1.718

3.11 Result of The Color Change

The color measurement results of the fabrics obtained after the wool fabric impregnating experiment of the 3e complex are given in Table 3.5.

The raw woolen fabric is already naturally yellowish and the yellowness grade is measured as 33.55. After the silver compound application, the yellow color of the wool with successive washings was somewhat reduced by the effect of washing. At the end of the 50 washings, the yellowness grade was measured as 31.79, so decreased by 2 points.

Table 3.5 : Color Measurement Results of Wool Fabric Applied Silver Compound According to Shooting Method (3d).

Sample Name	L*	a*	b*	WI (E 313 D65/10)	YI (E 313 D65/10)	C*	h*
Raw Wool Fabric	86.43	-0.27	17.87	-18.91	33.55	17.87	90.85
Without binder Unprocessed	85.89	-0.6	16.95	-16.02	31.86	16.96	92.02
Without binder 5. Washing	86.33	-0.19	18.60	-23.99	35.01	18.60	90.58
Without binder 10. Washing	86.33	-0.49	17.85	-19.16	33.36	17.86	91.56
Without binder 20. Washing	84.61	0.00	17.24	-20.89	33.23	17.24	90.01
Without binder 30. Washing	86.11	-0.19	16,80	-14.61	31.89	16.81	90.64
Without binder 40. Washing	84.88	-0.01	16.50	-16.50	31.86	16.50	90.03
Without binder 50. Washing	83.20	0.11	16.12	-19.19	31.79	16.12	89.60

3.12 Time Dependent Color Change

Wool fabric has been measured (immediately after application, after 3 month) stwice for whiteness. Color measurement was made for silver complex aplied wool fabrics with pulling method. The results showed that yellow color range has increased one point. It was thought that silver on surface results in color increase. That color change doesnt effect usage and esthetic properties of fabric.

Table 3.6 : Time Dependent Color Change Measurement Results (3d).

Sample Name	YI (E 313 D65/10) (Initial measurement)	YI (E 313 D65/10) (3 months later)
Control (raw)	3355	34.76
Without binder Unprocessed	31.86	32.78
5 washing without binders	35.01	36.65
10 washing without binders	33.36	34.78
20 washing without binders	33.23	34.87
30 washing without binders	31.89	32.54
40 washing without binders	31.86	32.45
50 washing without binders	31.79	32.98

3.13 Result of Hydrophilicity Measurement

The hydrophilicity values of the samples prepared with the 3d complex from the wool fabric studies are given in Table 3.7.

When the hydrophilicity of the raw hydrophilic wool fabric and hydrophilic values of the silver compound-applied fabrics are compared according to the shooting method; The hydrophilicity value of the raw wool fabric is 48 mm and the hydrophilicity value of the fabric without binder is 45. Hydrophilicity value decreased by 3 points. In successive washings, the hydrophilicity value improves by 1-2 points. While the hydrophilic values of the non-woven silver composite wool fabrics decrease slightly, this decrease is not so significant as to change the use characteristics of the fabric.

Table 3.7 : Hydrophilicity Test Results of Silver Appliqued Wool Fabric with Shooting(3d).

Fabrics	Hydrophilicity (s)
Crude	48
Without binder unprocessed	45
Without binder 5. Washing	45
Without binder 10. Washing	45
Without binder 20. Washing	46
Without binder 30. Washing	46
Without binder 40. Washing	47
Without binder 50. Washing	47

4. CONCLUSION

FT-IR, ^{1}H-NMR and ^{13}C-NMR spectra, the synthesis of imidazole derivatives was successful**.** Showed the best effect '3d' complex among the synthesized compounds. For this reason, this molecule was immobilized to farbric. A homogeneous distribution is not observed in wool fabrics impregnated with 3d complex. In the randomly selected areas, the Ag amount is in the range of 0.26-0.58 % by weight. This shows us that the complex is impregnated on the fabric and that the impregnate rate is roughly applicable to the field of medical textiles.

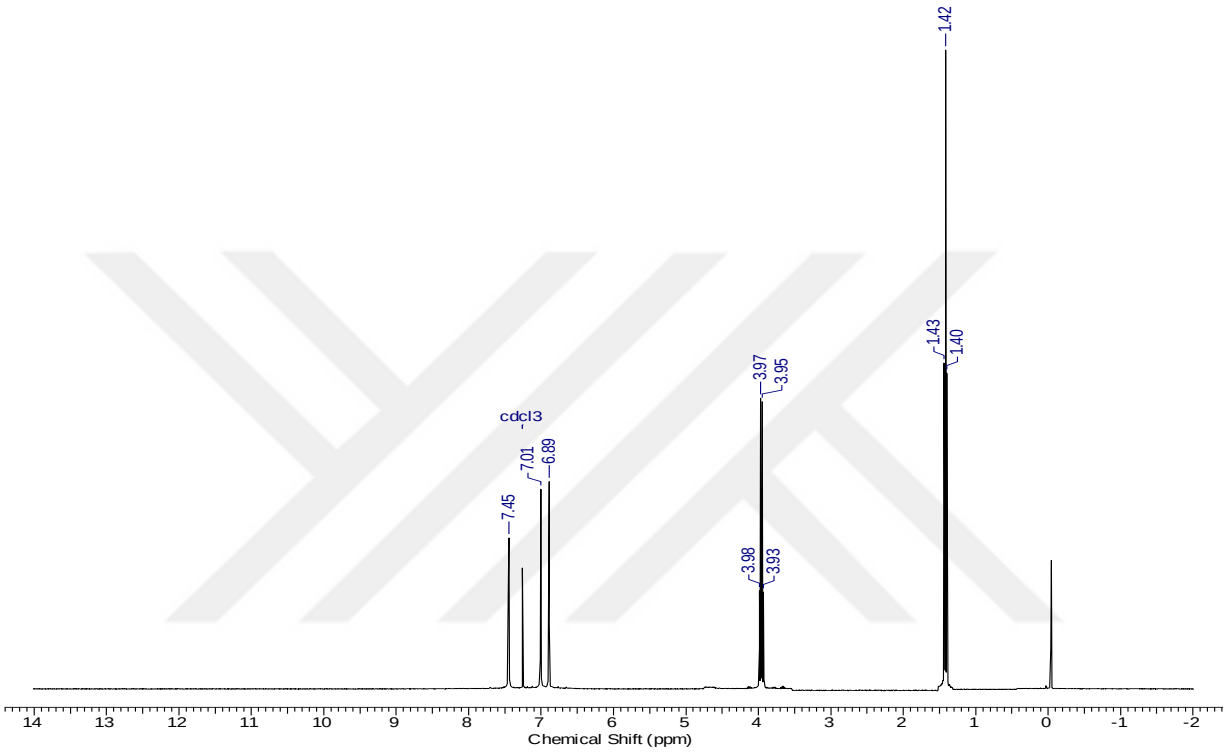
The raw woolen fabric is already naturally yellowish and the yellowness grade is measured as 33.55. After the silver compound application, the yellow color of the wool with successive washings was somewhat reduced by the effect of washing. At the end of the 50 washings, the yellowness grade was measured as 31.79, so decreased by 2 points.

After the silver compound application, the yellow color of the wool with successive washings was somewhat reduced by the effect of washing. At the end of the 50 washings, the yellowness grade was measured as 31.79, so decreased by 2 points. While the hydrophilic values of the non-woven silver composite wool fabrics decrease slightly, this decrease is not so significant as to change the use characteristics of the fabric.

It can be seen that the wool fabric applied with the silver compound (3d) according to the impregnation method shows 99.93% antibacterial activity against gram-positive S. aureus and 99.63% against gram-negative K.pneumoniae. The efficacy after 5 washes decreased to 99.17% against gram-positive S. aureus and 99.40% against gram-negative K.pneumoniae. At the end of 30 washes the efficacy decreased to 97.74% against gram-positive S. aureus and to 66.55% against gram-negative K.pneumoniae. At the end of 50 washes, the activity decreased to 97.65% against gram-positive S. aureus and to 65.17% against gram-negative K. pneumoniae. From here it appears that silver compound is more effective against gram-positive S. aureus.

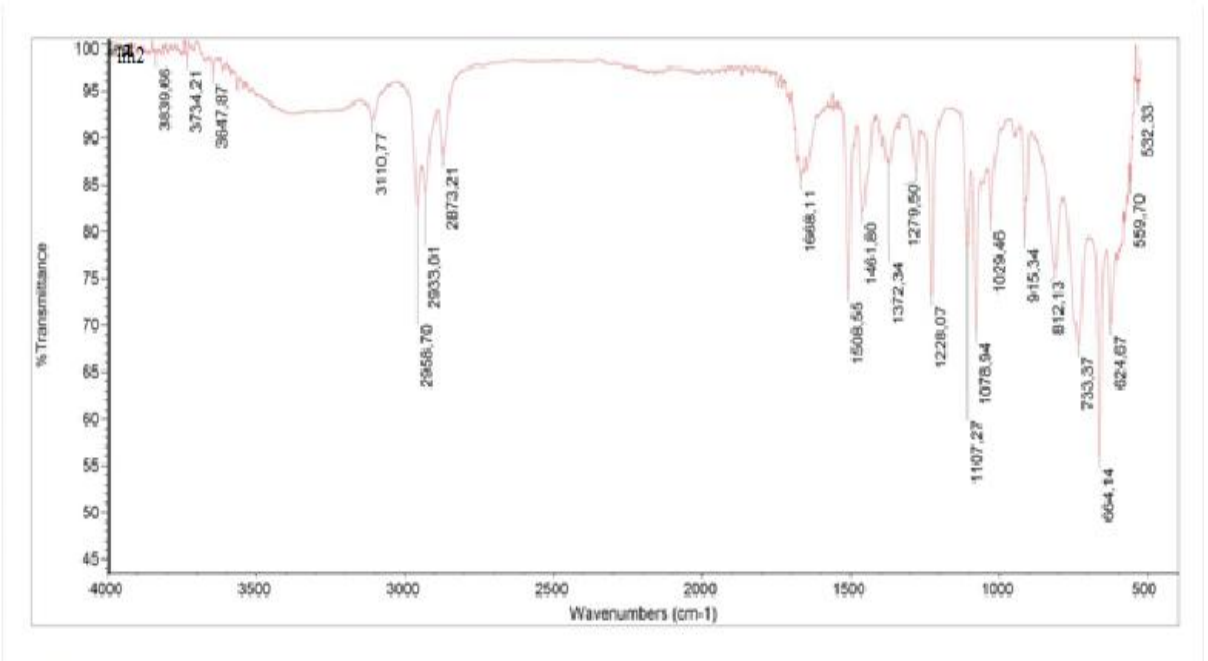
5. APPENDICES

1.



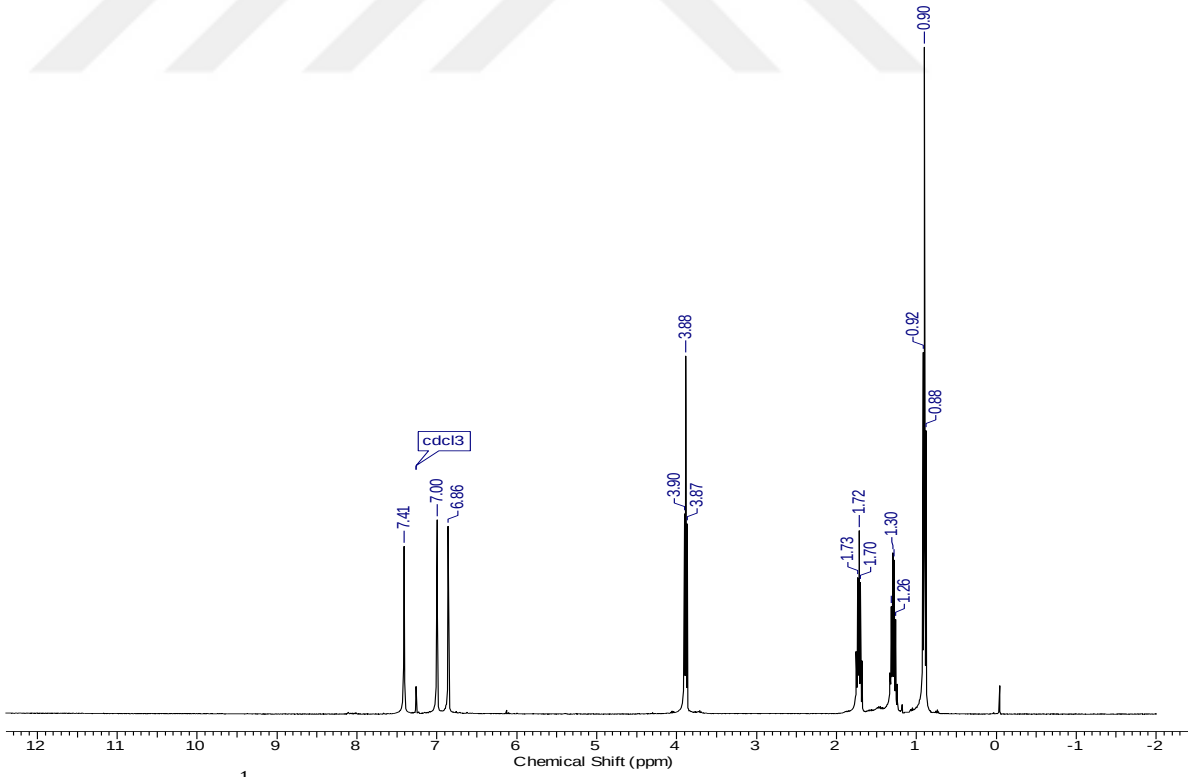
Appendice 1 The H^1NMR Spectrum of 1a [1-ethyl-1*H*-imidazole].

2.



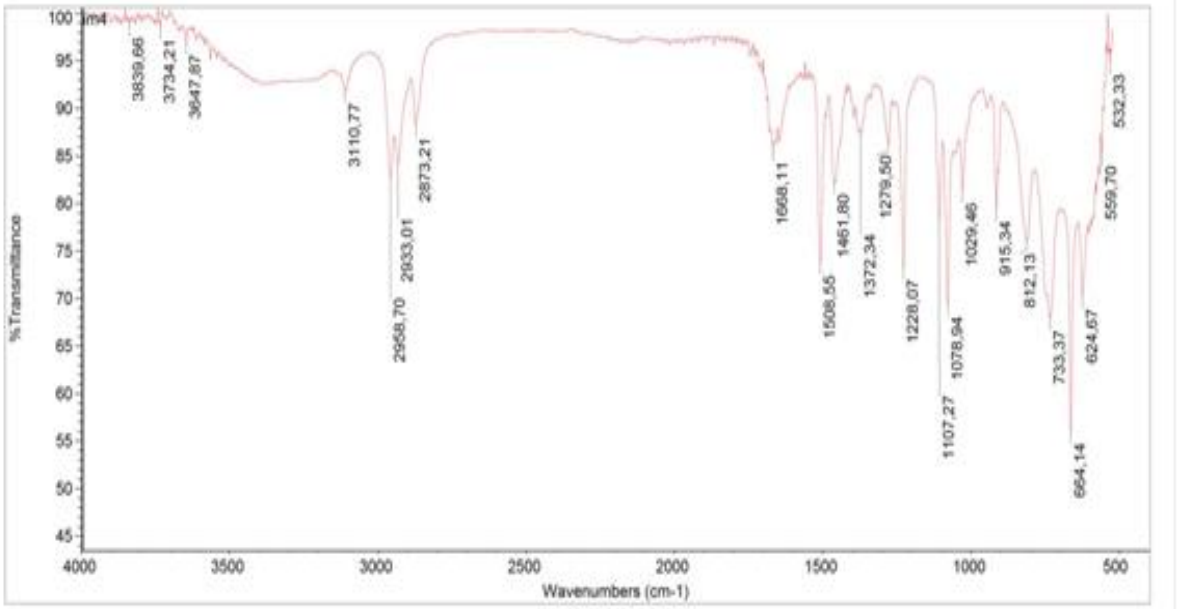
Appendice 2 The FT-IR Spectrum of 1a [1-ethyl-1*H*-imidazole].

3.



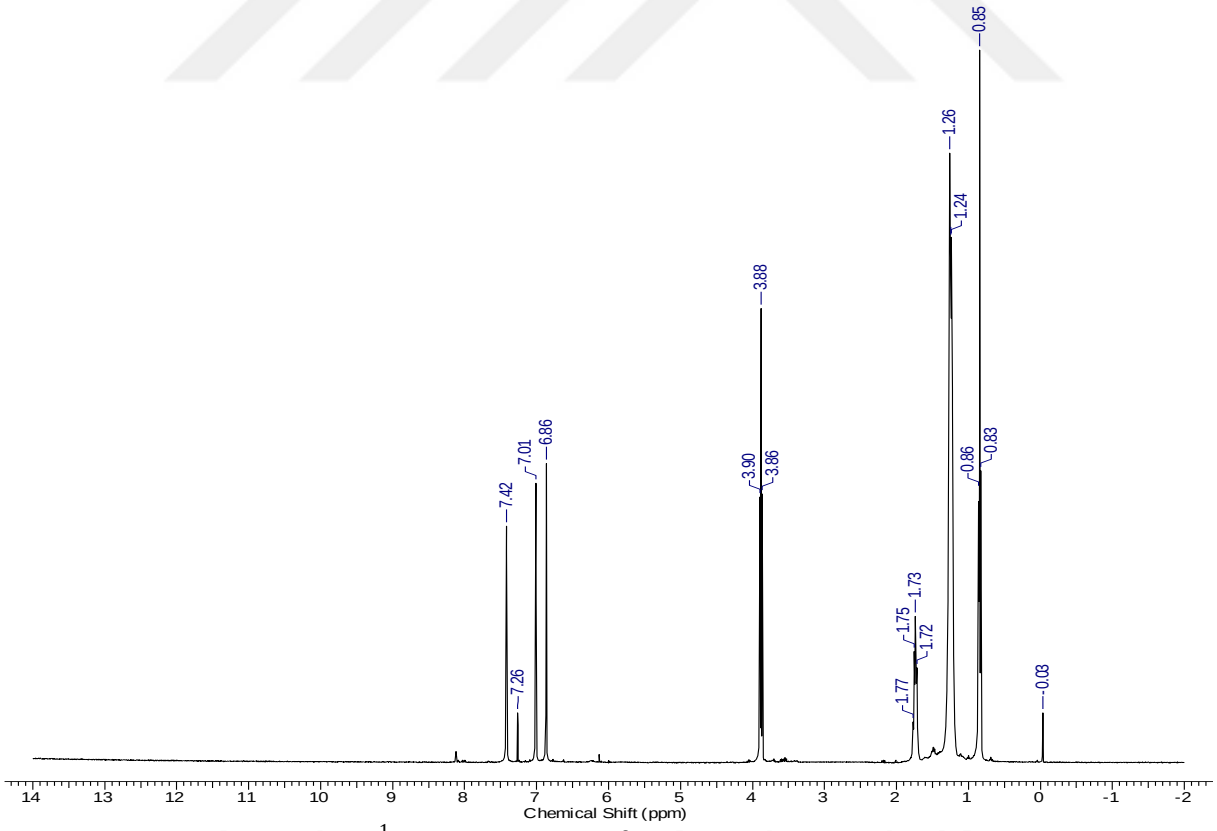
Appendice 3 The H^1NMR spectrum of 1b[1-butyl-1*H*-imidazole].

4.



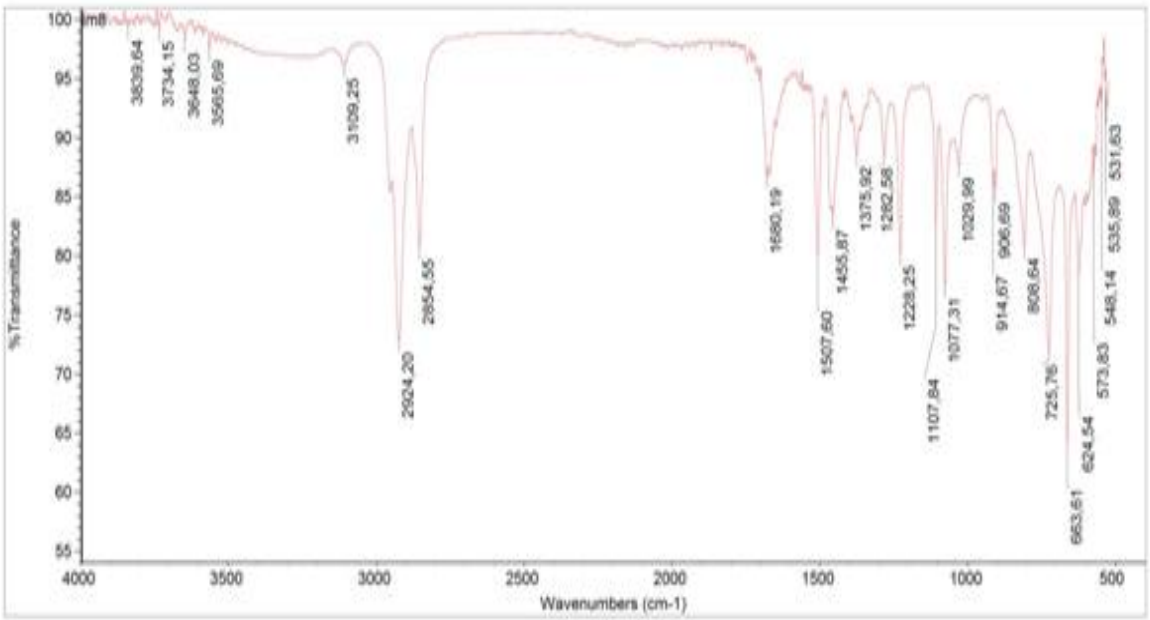
Appendice 4 The FT-IR Spectrum of 1b [1-butyl-1*H*-imidazole].

5.



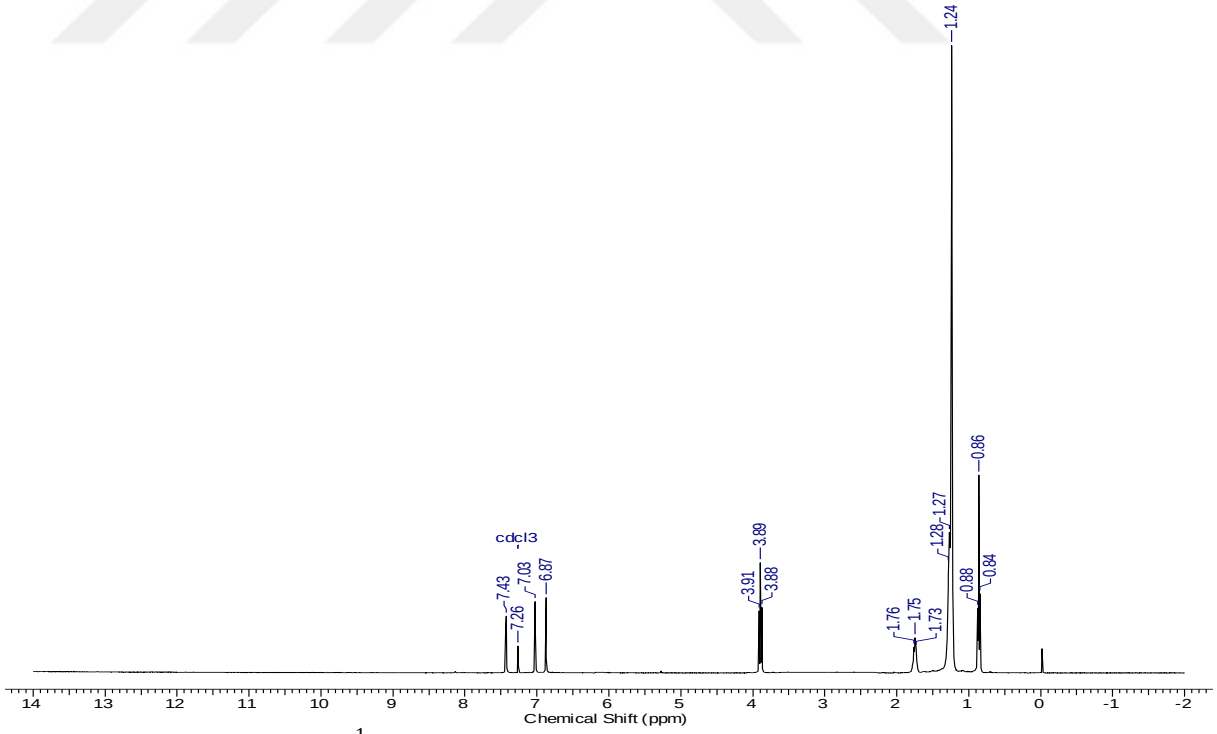
Appendice 5 The H^1NMR Spectrum of 1c [1-octyl-1*H*-imidazole].

6.



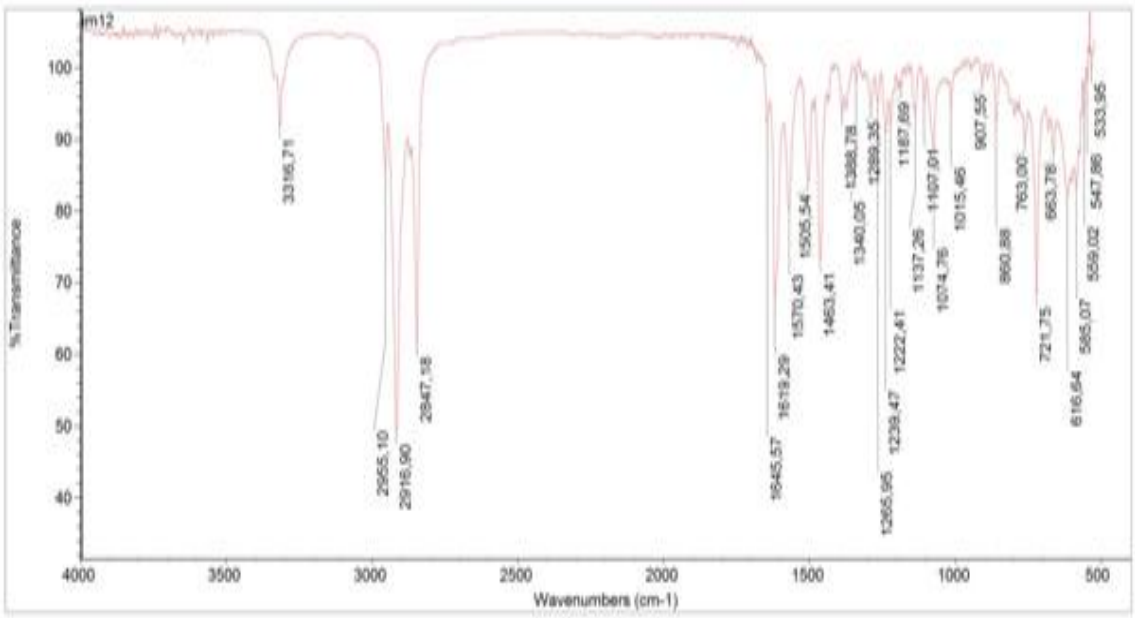
Appendice 6 The FT-IR Spectrum of 1c [1-octyl-1*H*-imidazole].

7.



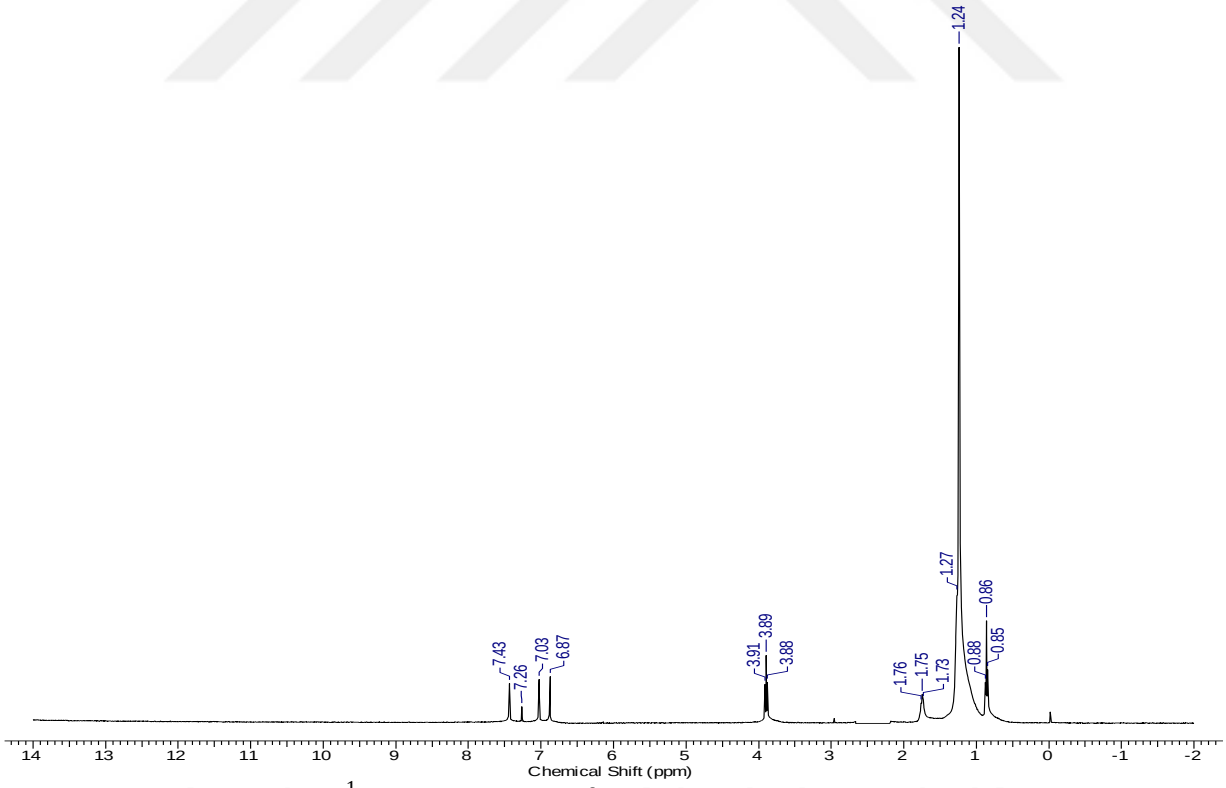
Appendice 7 The H^1NMR Spectrum of 1d [1-dodectyl-1*H*-imidazole].

8.



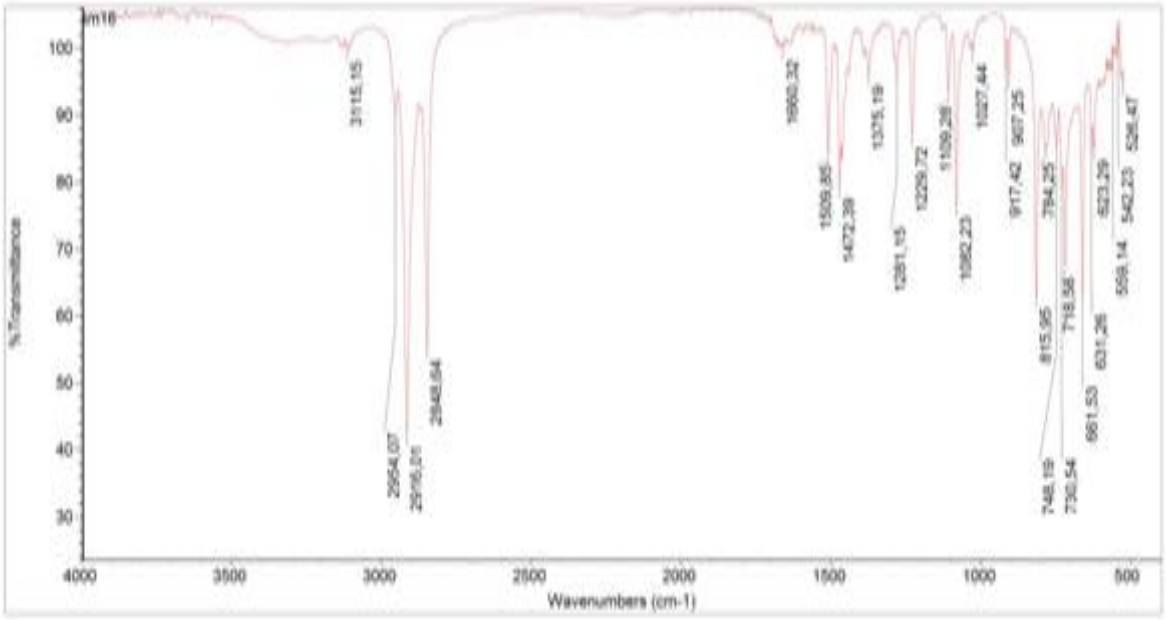
Appendice 8 The FT-IR Spectrum of 1d [1-dodecyl-1*H*-imidazole].

9.



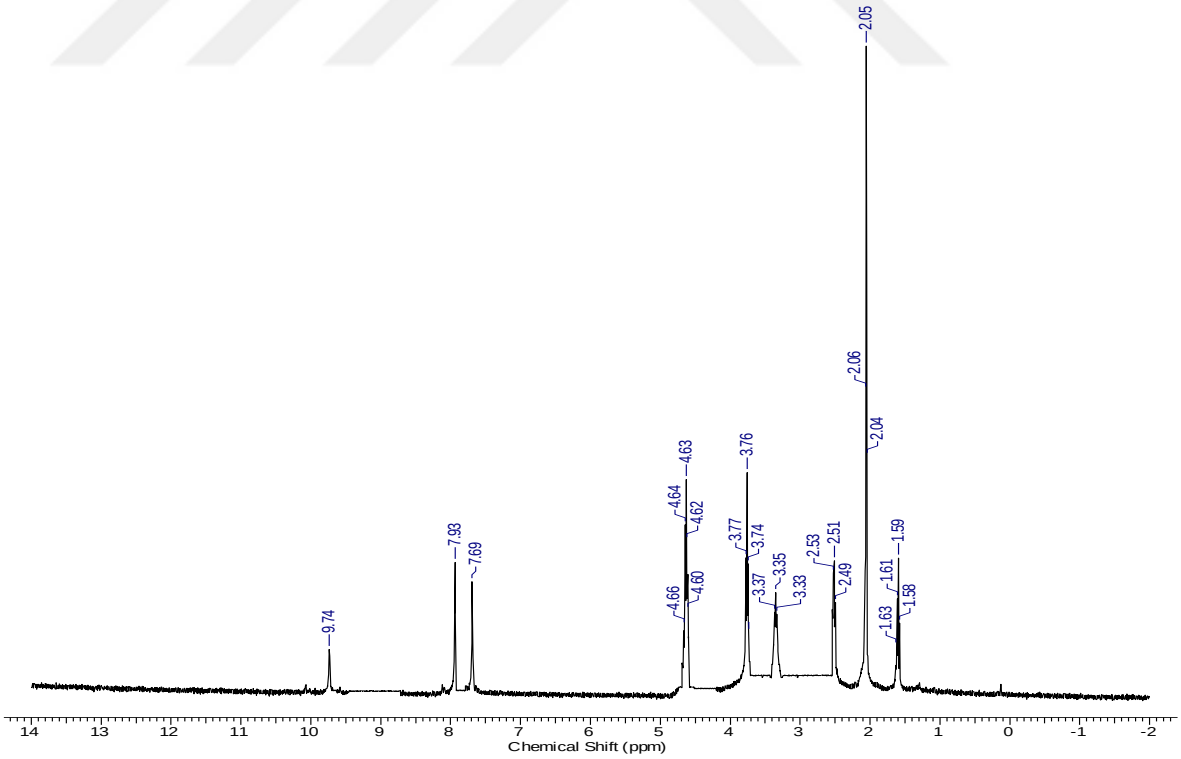
Appendice 9 The H[1]NMR Spectrum of 1e [1-hexadecyl-1*H*-imidazole].

10.



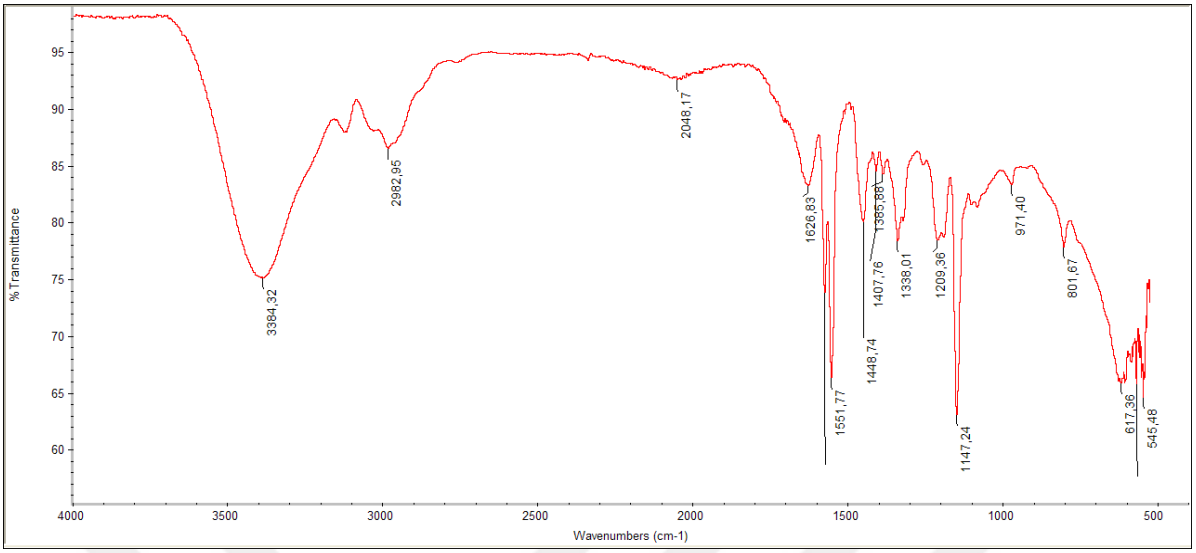
Appendice 10 The FT-IR Spectrum of 1e [1-hexadecyl-1*H*-imidazole].

11.



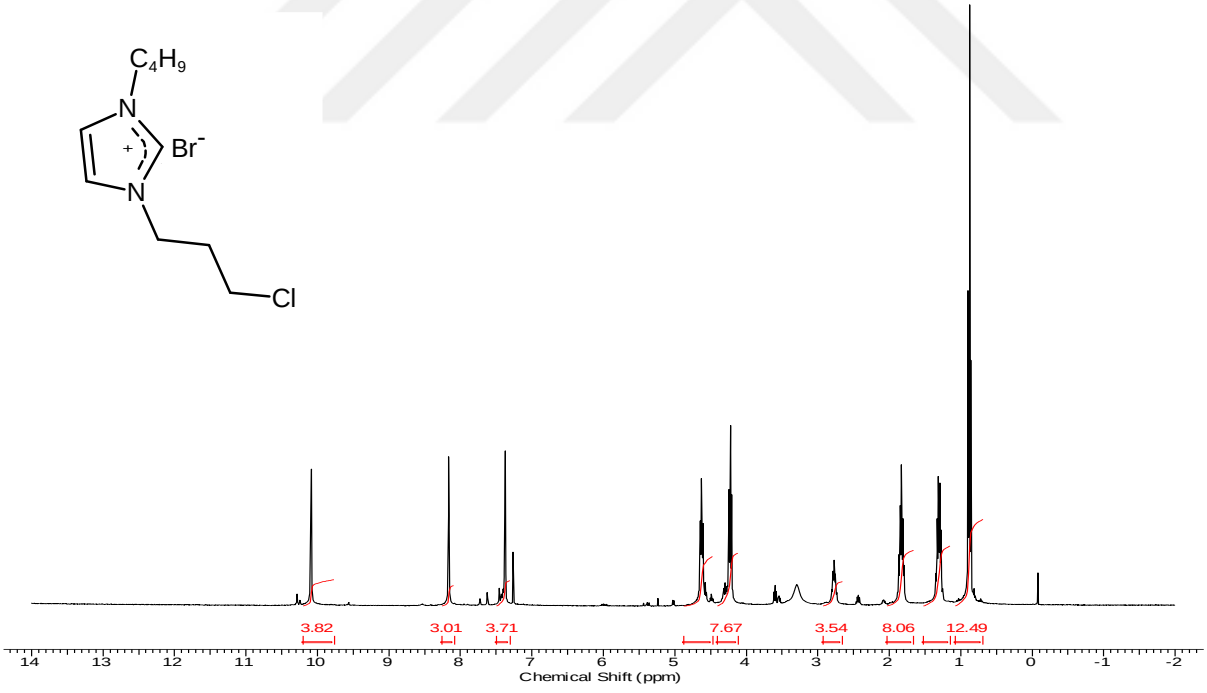
Appendice 11 The H^1NMR Spectrum of 2a [1-ethyl-3-(3-chloropropil)imidazolium bromide].

12.



Appendice 12 The FT-IR Spectrum of 2a [1-ethyl-3-(3-chloropropil)imidazolium bromide].

13.



Appendice 13 The H^1NMR Spectrum of 2b [1-butyl-3-(3-chloropropil)imidazolium bromide].

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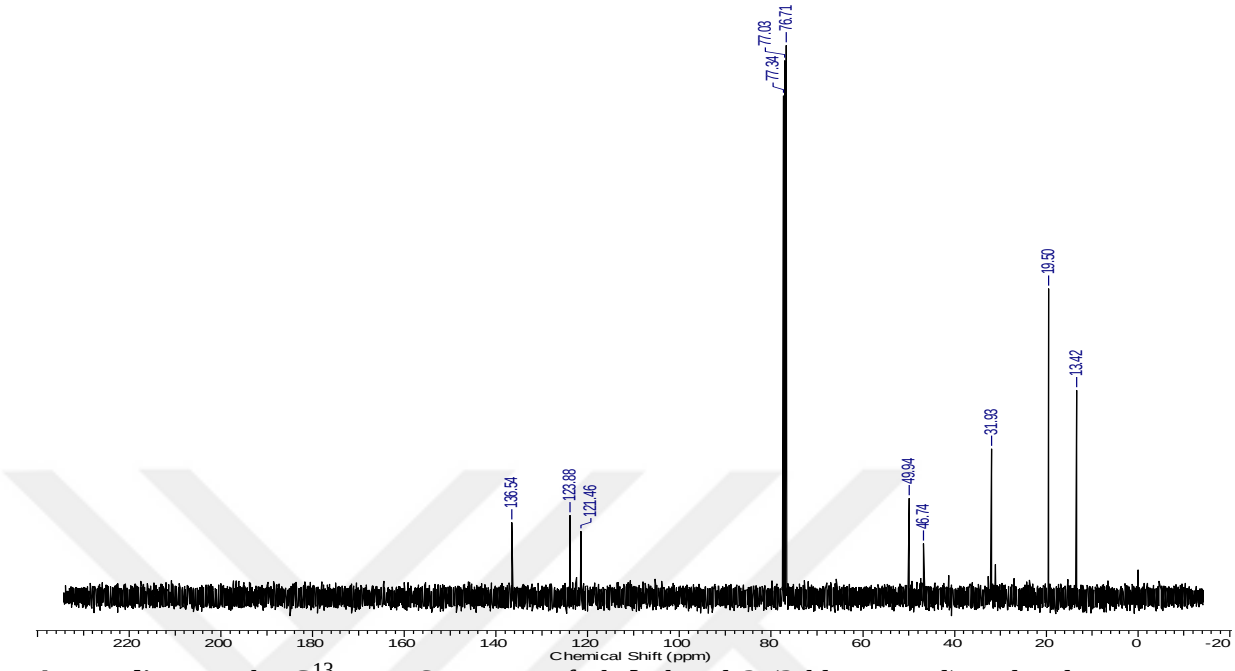
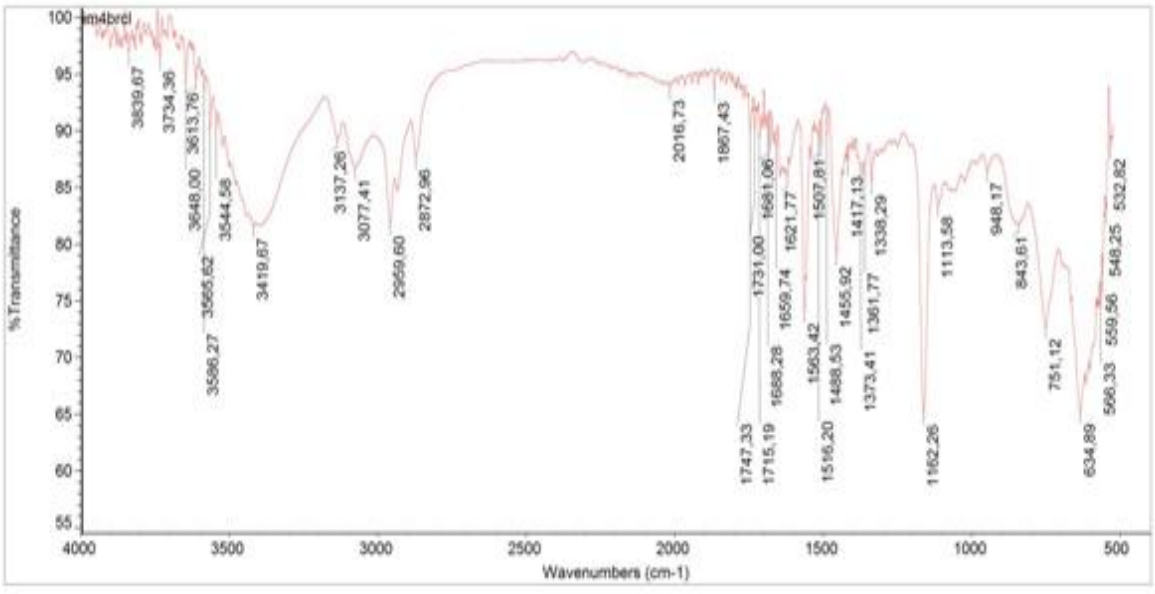


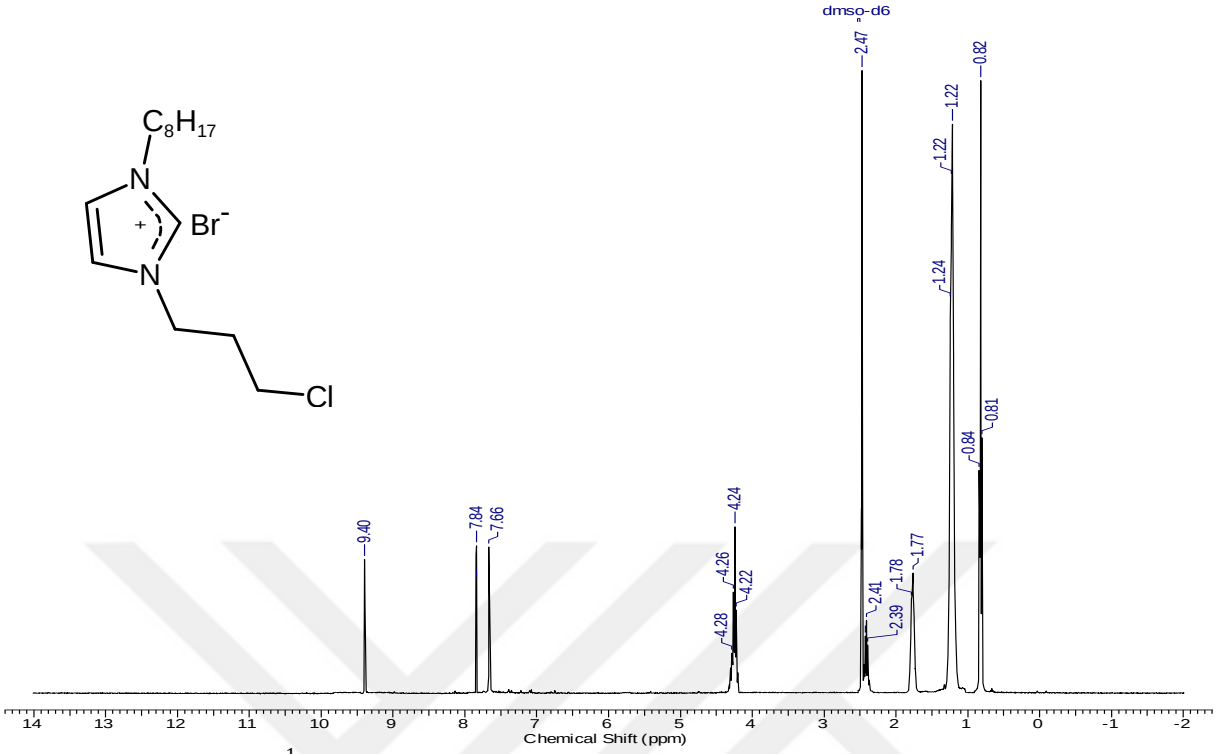
Appendice 14 The C^{13}NMR Spectrum of 2b [1-butyl-3-(3-kloropropil)imidazolyum bromür].

15.



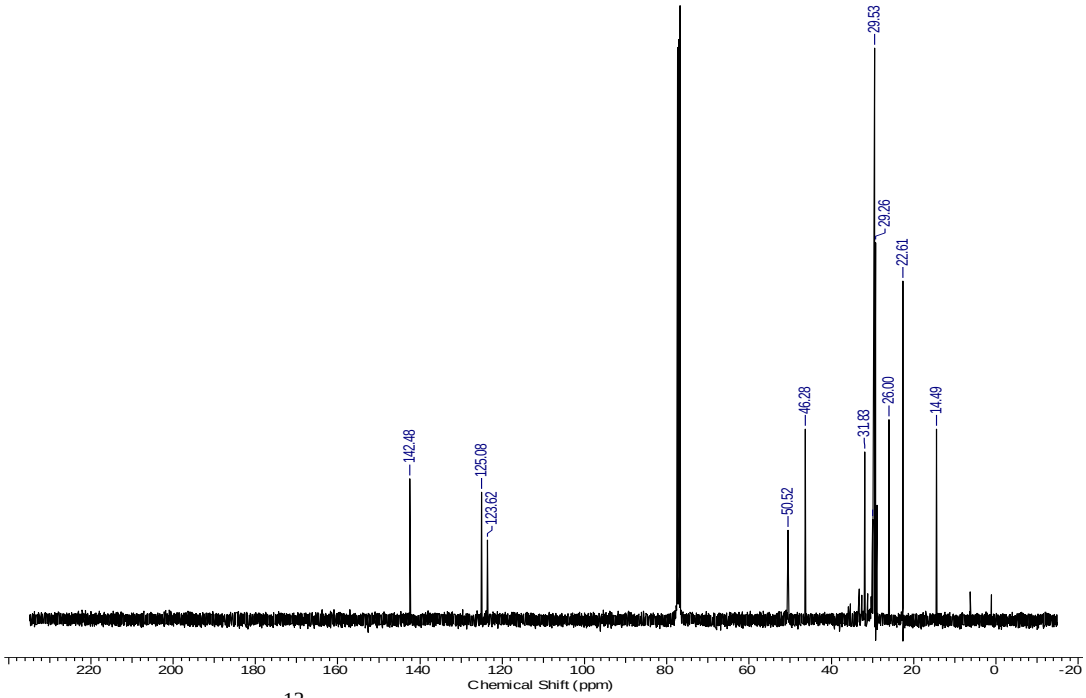
Appendice 15 The FT-IR Spectrum of 2b [1-butyl-3-(3-chloropropil)imidazolium bromide].

16.



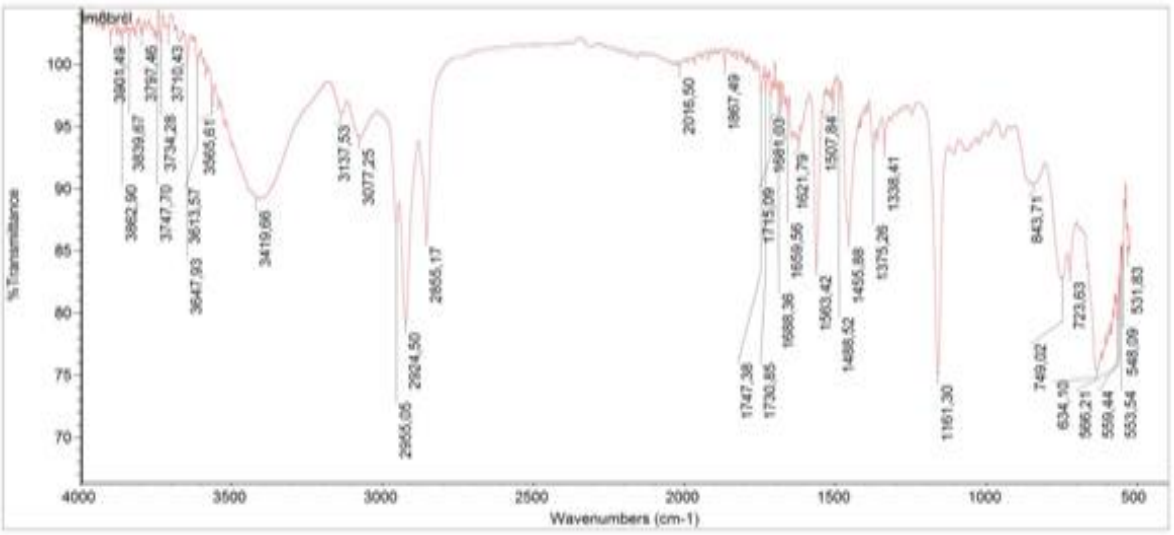
Appendice 16 The H^1NMR Spectrum of 2c [1-octyl-3-(3-chloropropil)imidazolium bromide].

17.



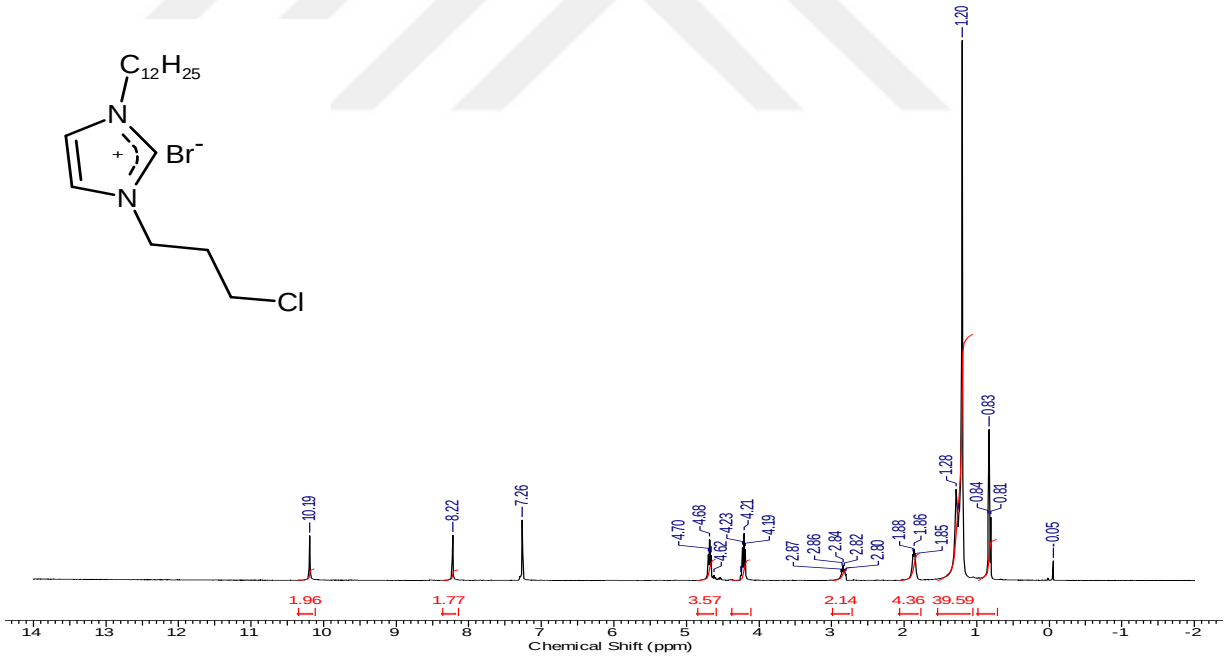
Appendice 17 The C^{13}NMR Spectrum of 2c [1-octyl-3-(3-kloropropil)imidazolyum bromür].

18.



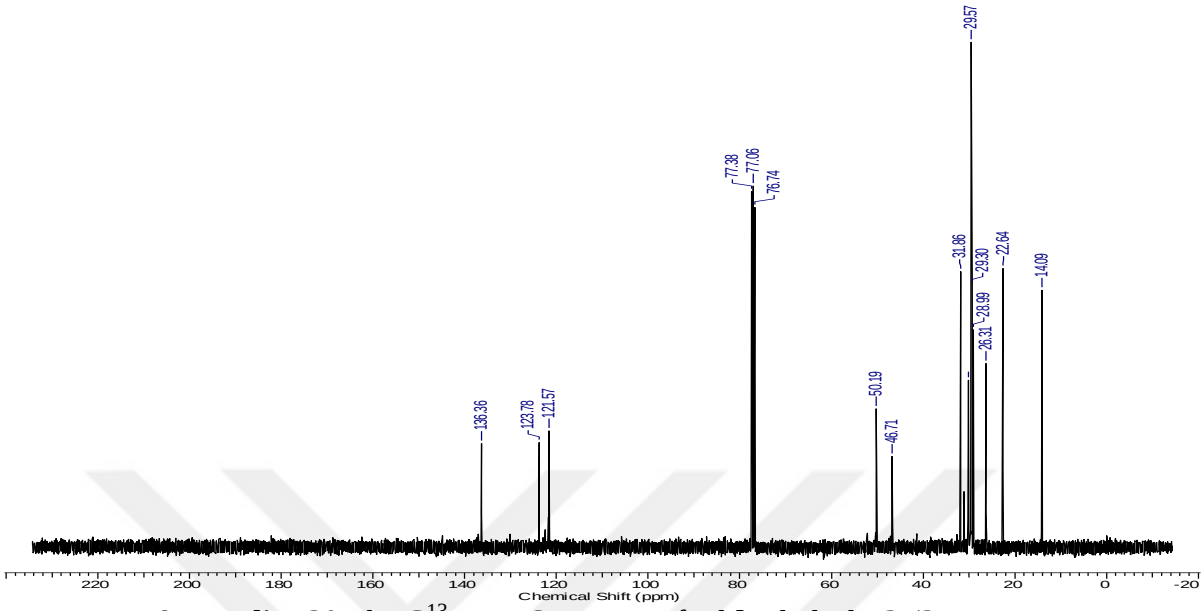
Appendice 18 The FT-IR Spectrum of 2c [1-octyl-3-(3-chloropropil)imidazolium bromide].

19.



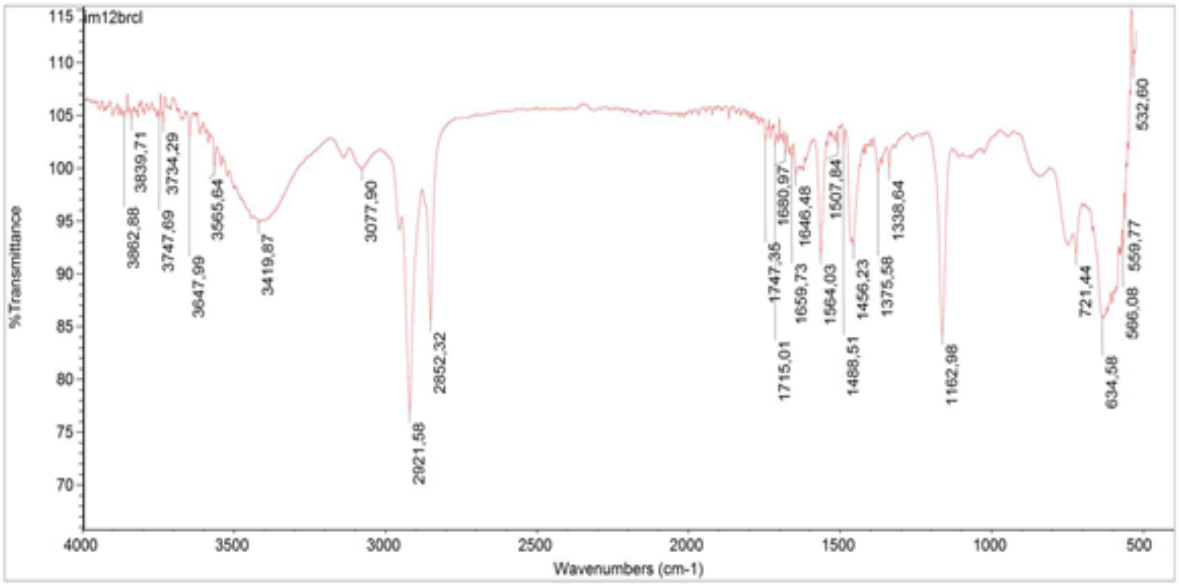
Appendice 19 The H^1NMR Spectrum of 2d [1-dodecyl-3-(3-chloropropil)imidazolium bromide].

20.



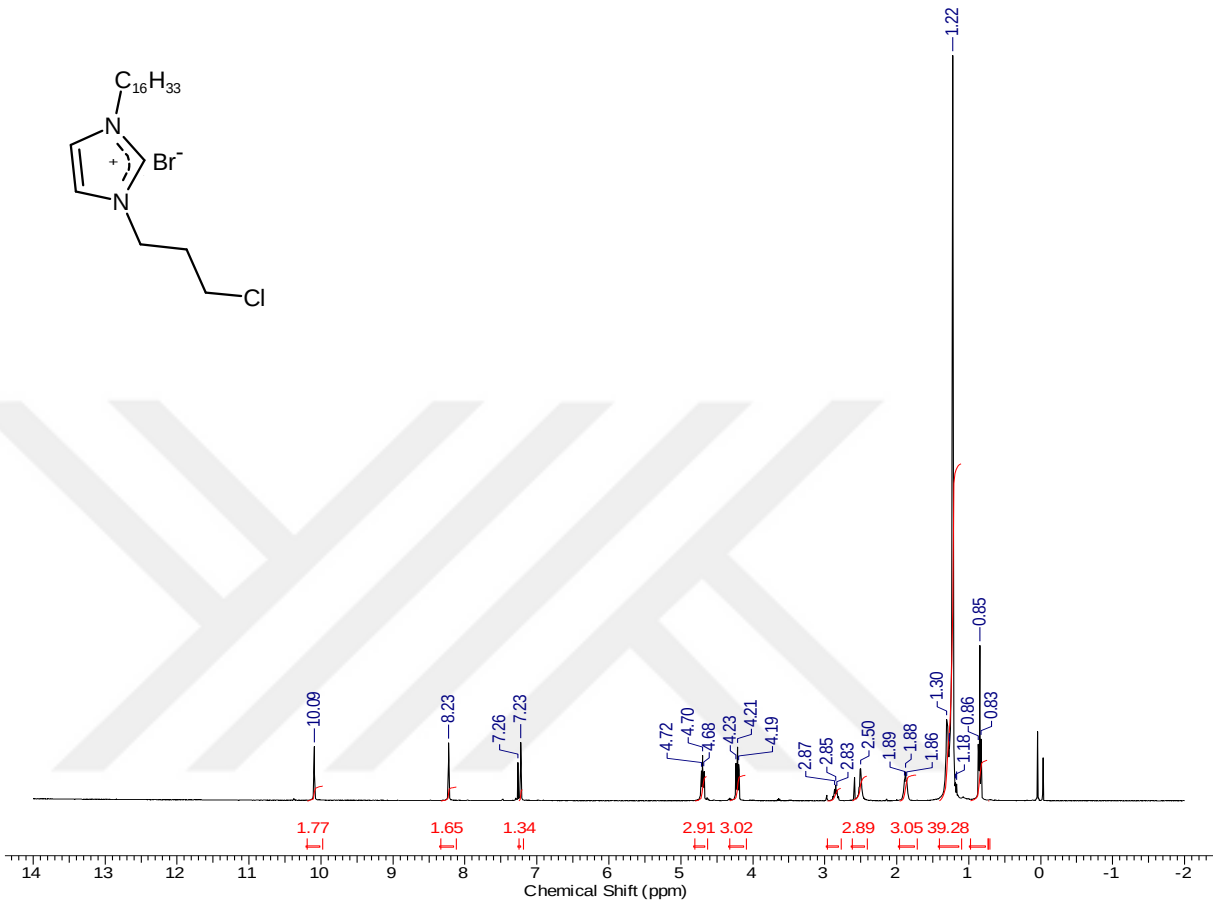
Appendice 20 The C^{13}NMR Spectrum of 2d [1-dodecly-3-(3-chloropropil)imidazolium bromide].

21.



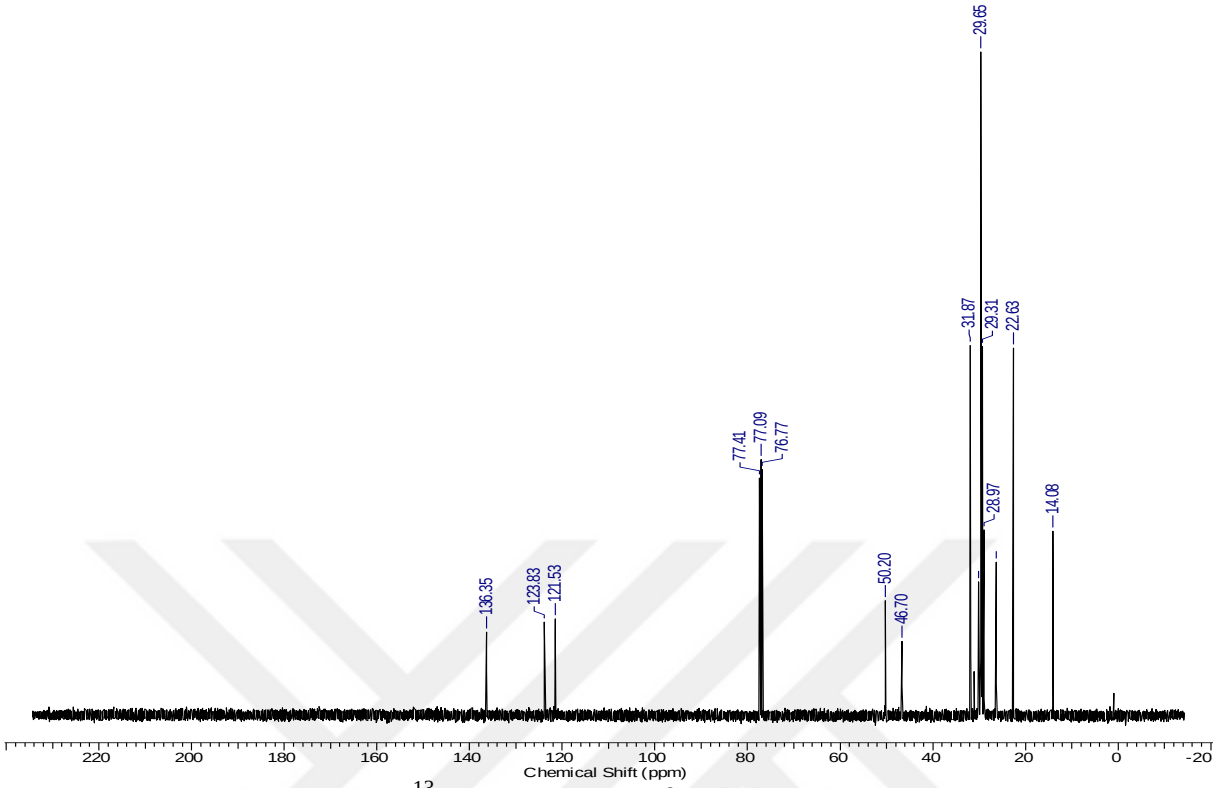
Appendice 21 The FT-IR Spectrum of 2d [1-dodecyl-3-(3-kloropropil)imidazolyum bromür].

22



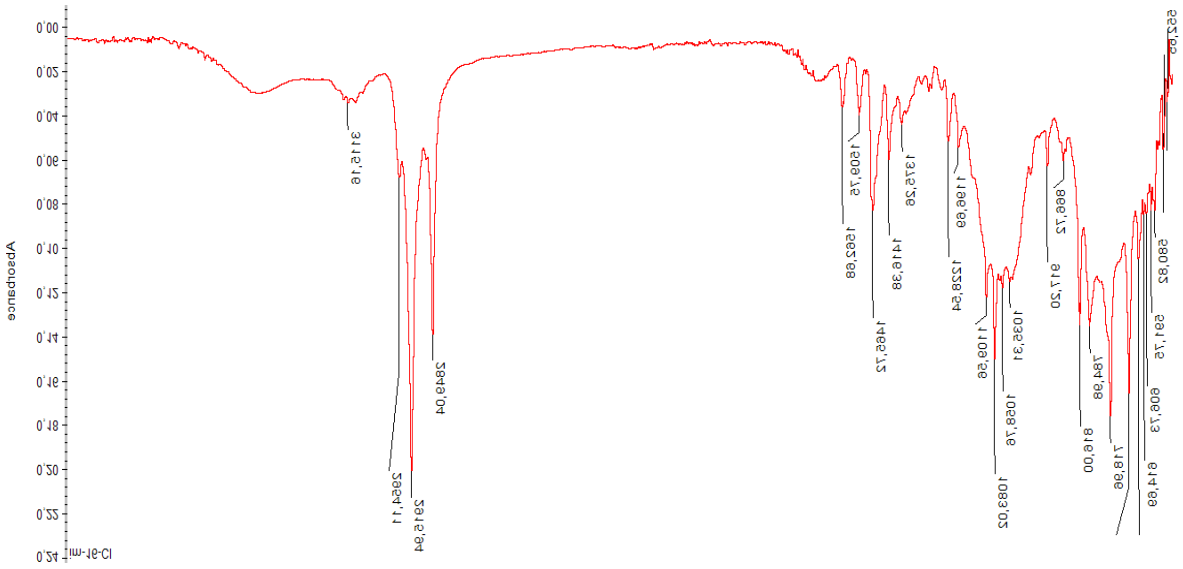
Appendice 22 The H^1NMR Spectrum of 2e [1-hexadecyl-3-(3-chloropropil)imidazolium bromide].

23.



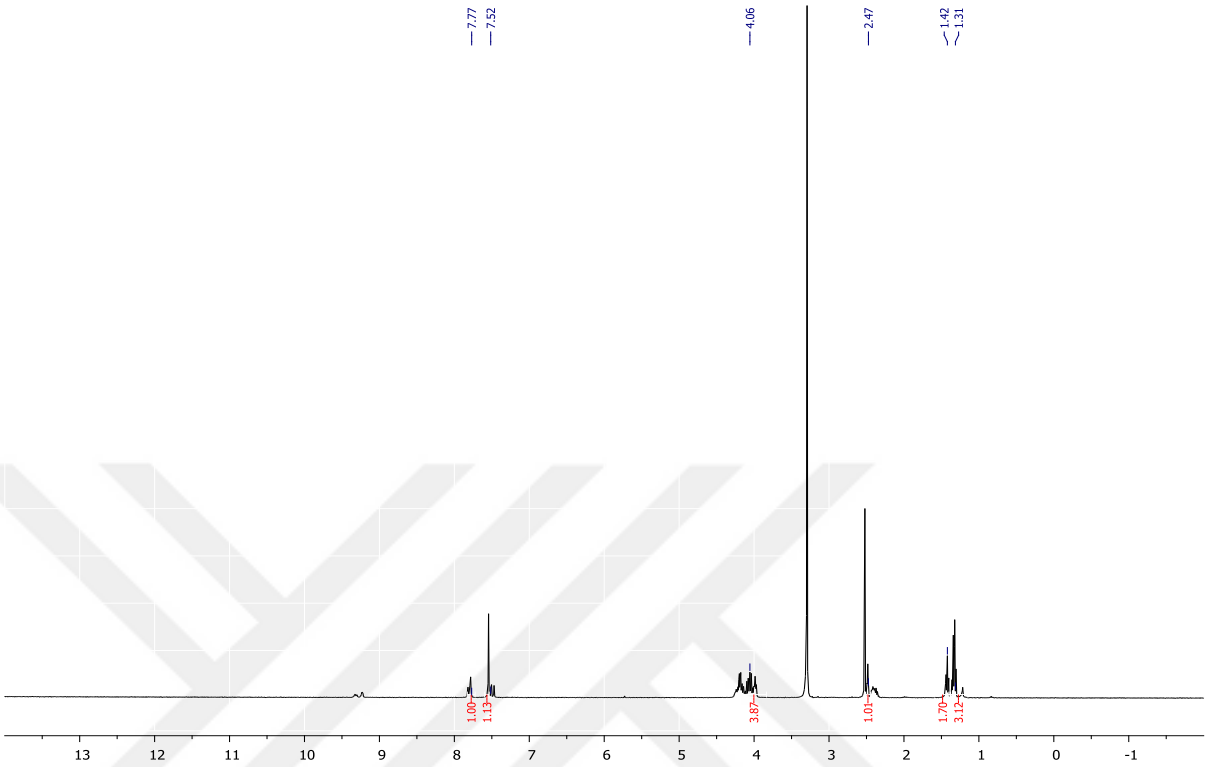
Appendice 23 The C^{13}NMR Spectrum of 2e [1-hexadecyl-3-(3-chloropropil)imidazolium bromide].

24.



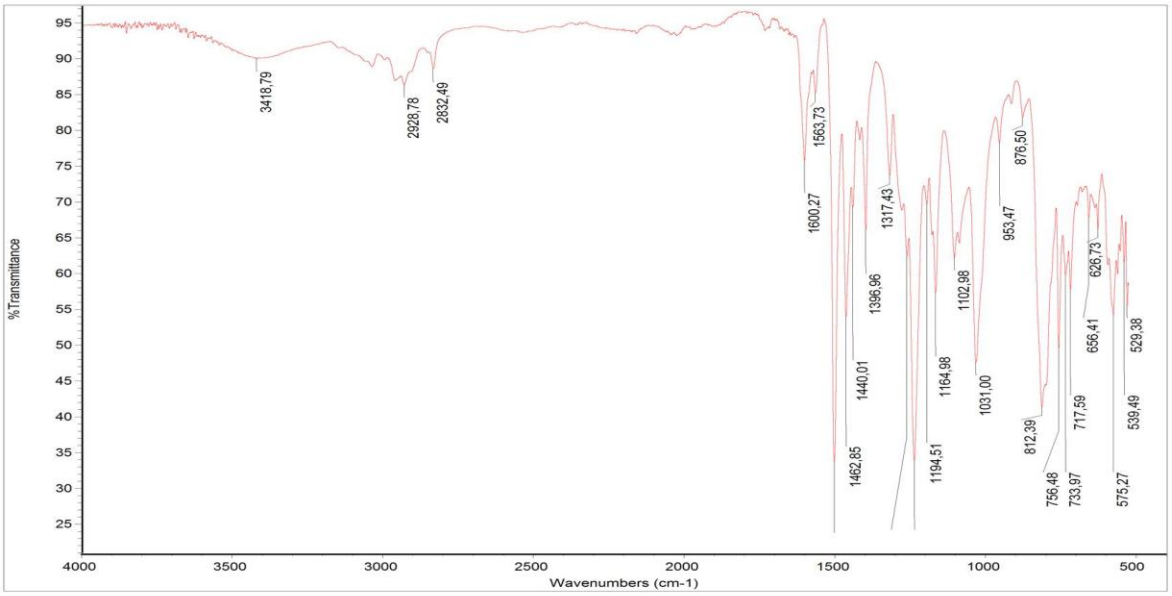
Appendice 24 The FT-IR Spectrum of 2e [1-hexadecyl-3-(3-chloropropil)imidazolium bromide].

25.



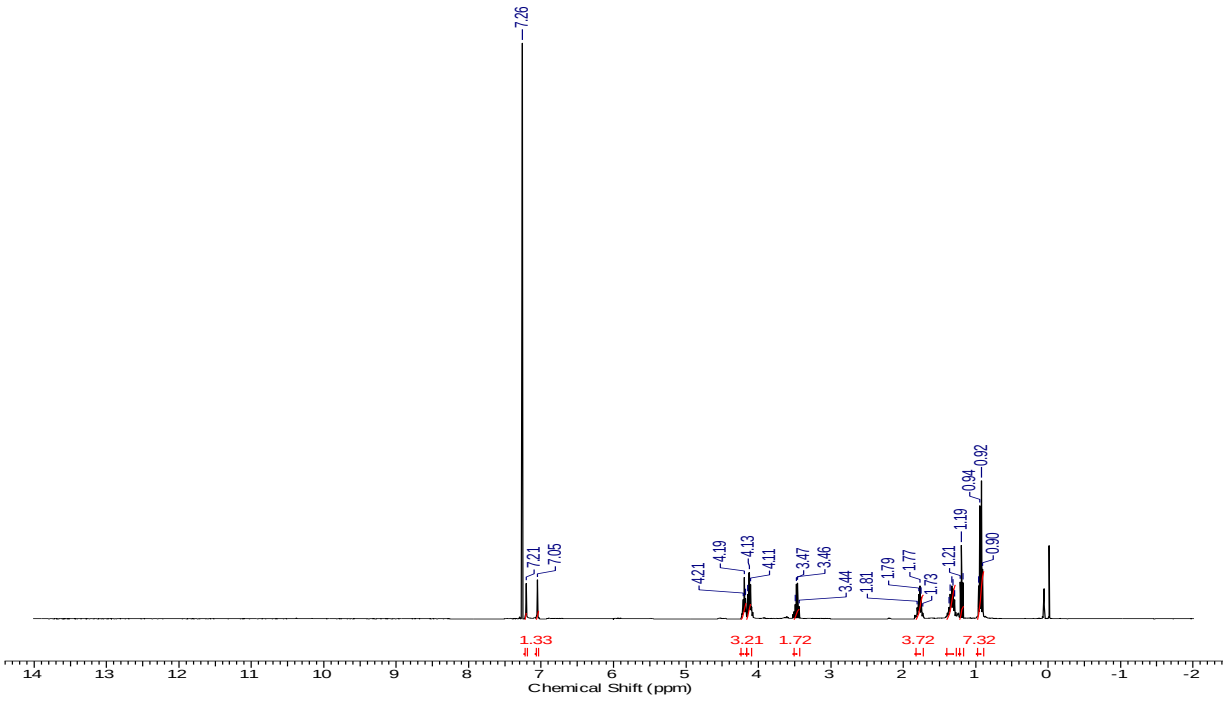
Appendice 25 The H^1NMR Spectrum of 3a [1-ethyl-3-(3-chloropropyl)-1H-imidazol-3-ium-2-yl]silver.

26.



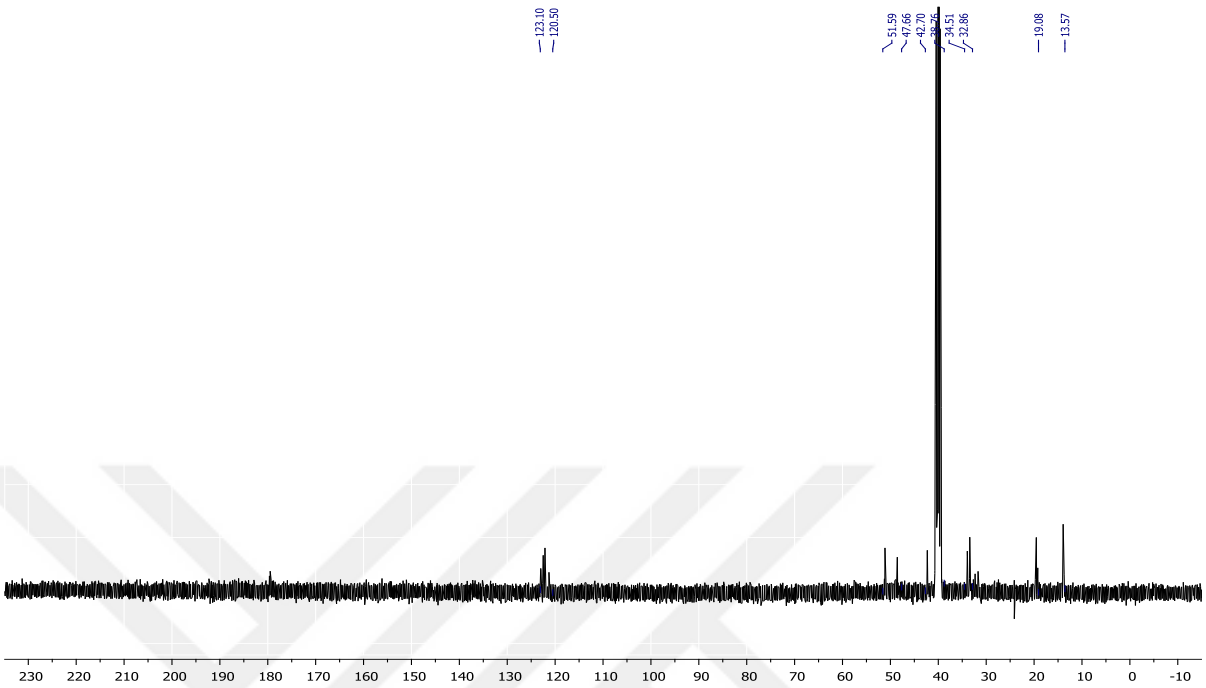
Appendice 26 The FT-IR Spectrum of 3a [1-ethyl-3-(3-chloropropyl)-1H-imidazol-3-ium-2-yl]silver.

27.



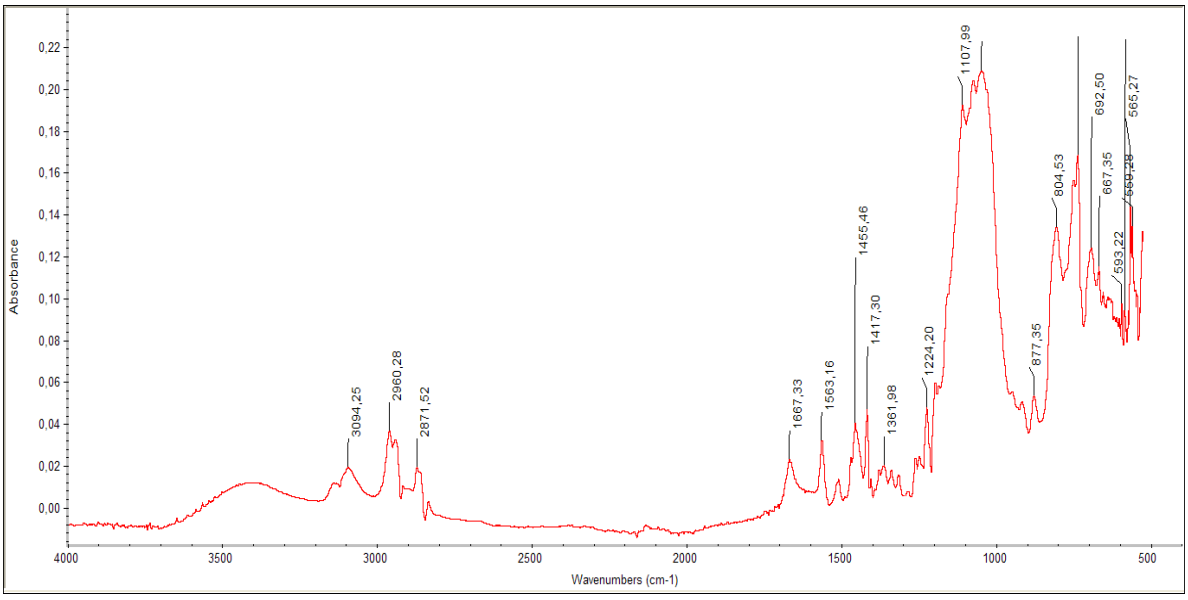
Appendice. 27 The H^1NMR Spectrum of 3b[1-butyl-3-(3-chloropropyl)-1H-imidazol-3-ium-2-yl]silver.

28.



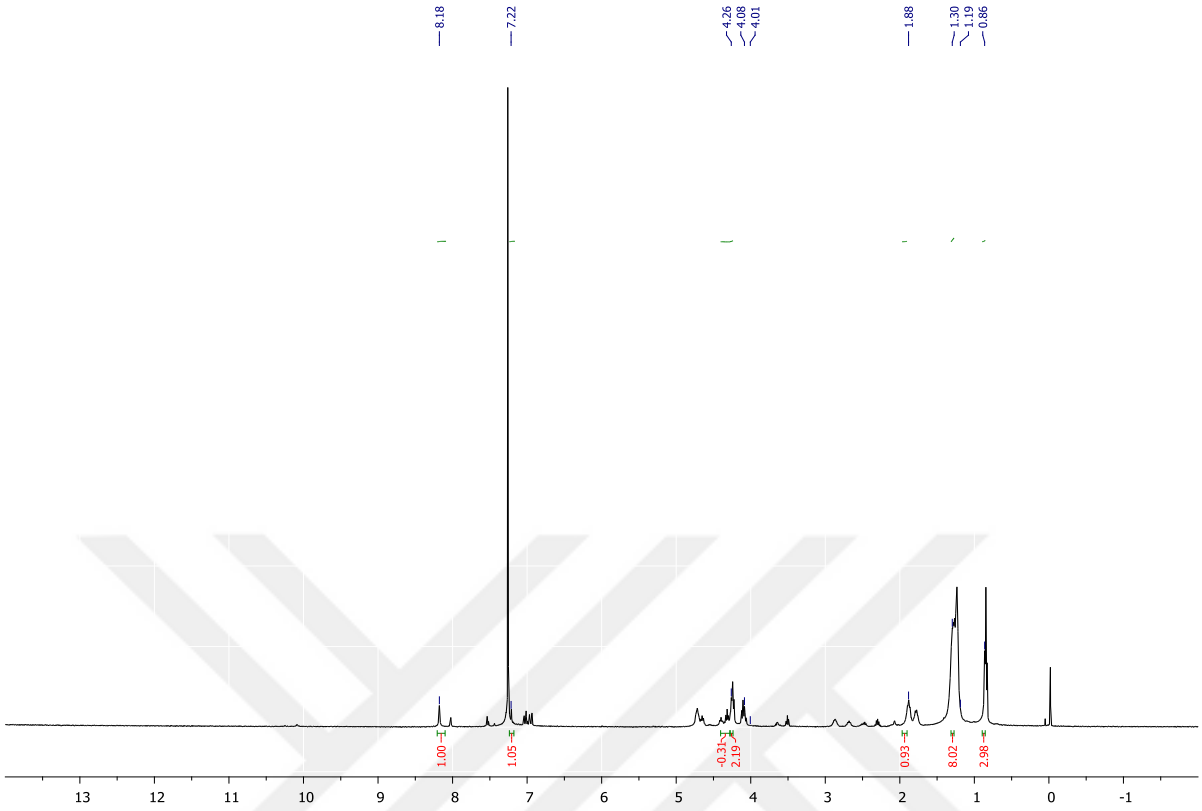
Appendice 28 The C^{13}NMR Spectrum of 3b [1-buthyl-3-(3-chloropropyl)-1H-imidazol-3-ium-2-yl]silver salt.

29.



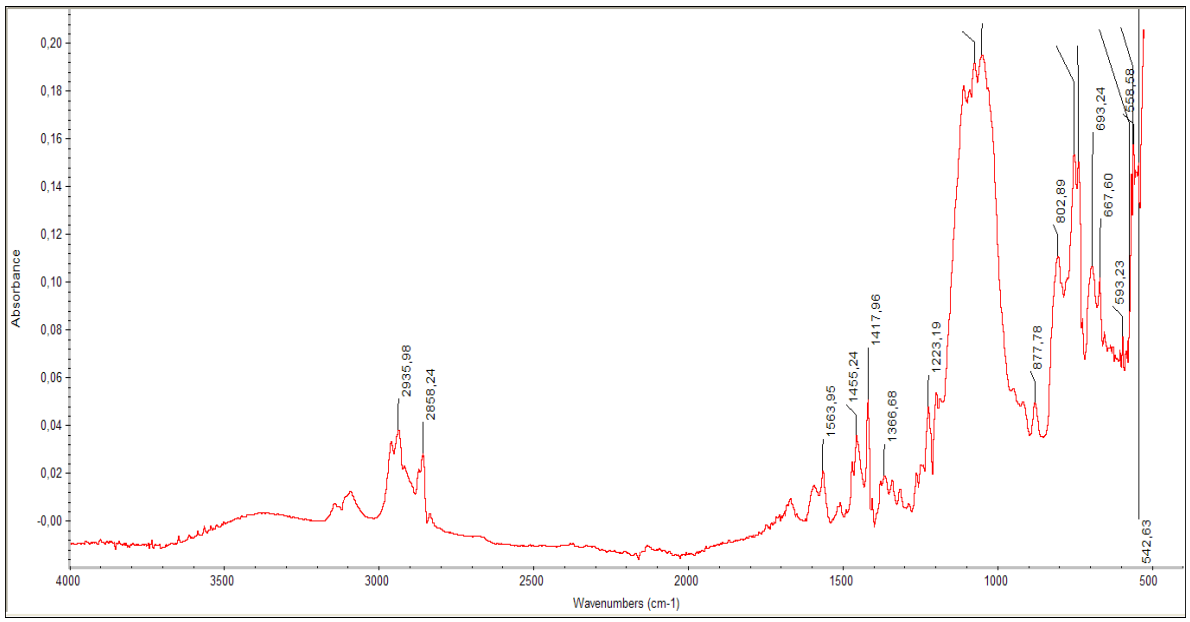
Appendice 29 The FT-IR Spectrum of 3b[1-butyl-3-(3-chloropropyl)-1H-imidazol-3-ium-2-yl]silver.

30.



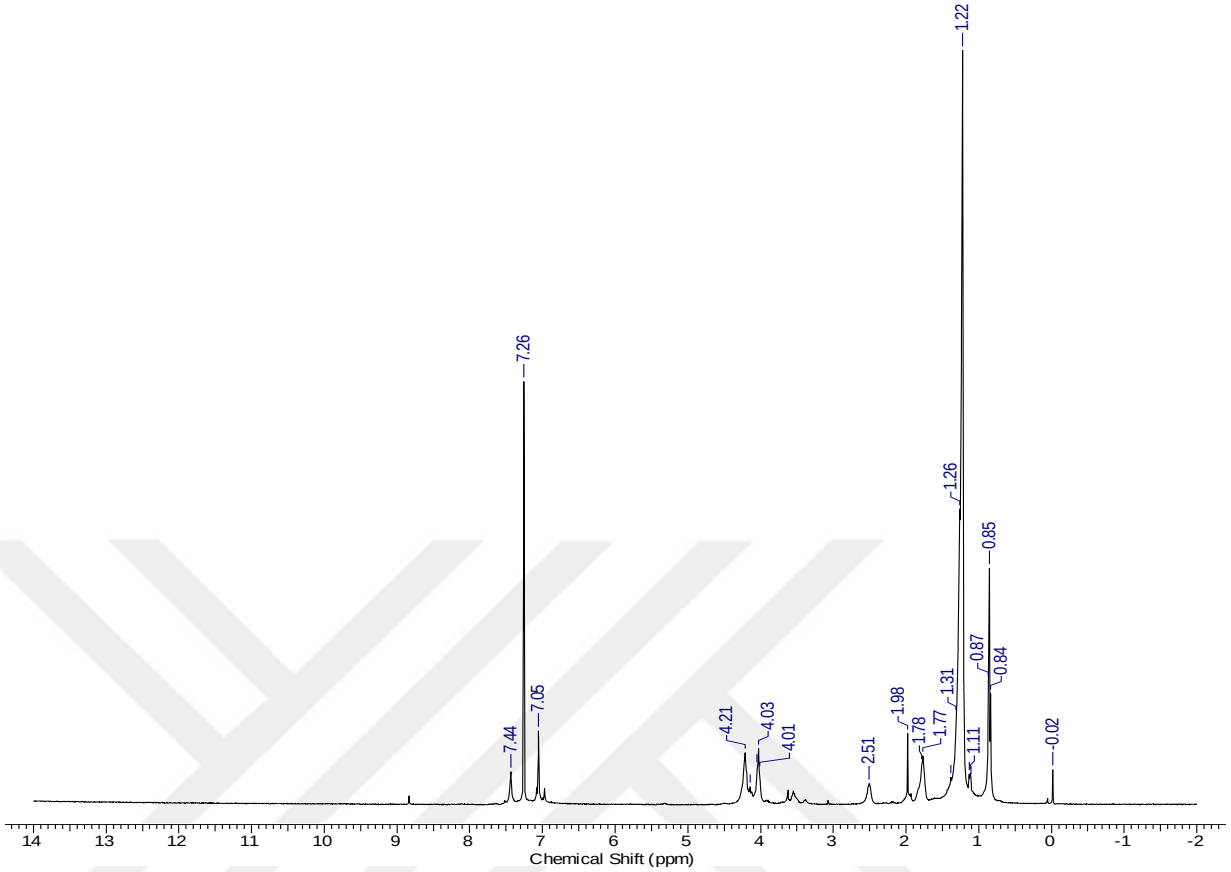
Appendice 30 The H^1NMR Spectrum of 3c [1-octyl-3-(3-chloropropyl)-1H-imidazol-3-ium-2-yl]silver salt.

31.



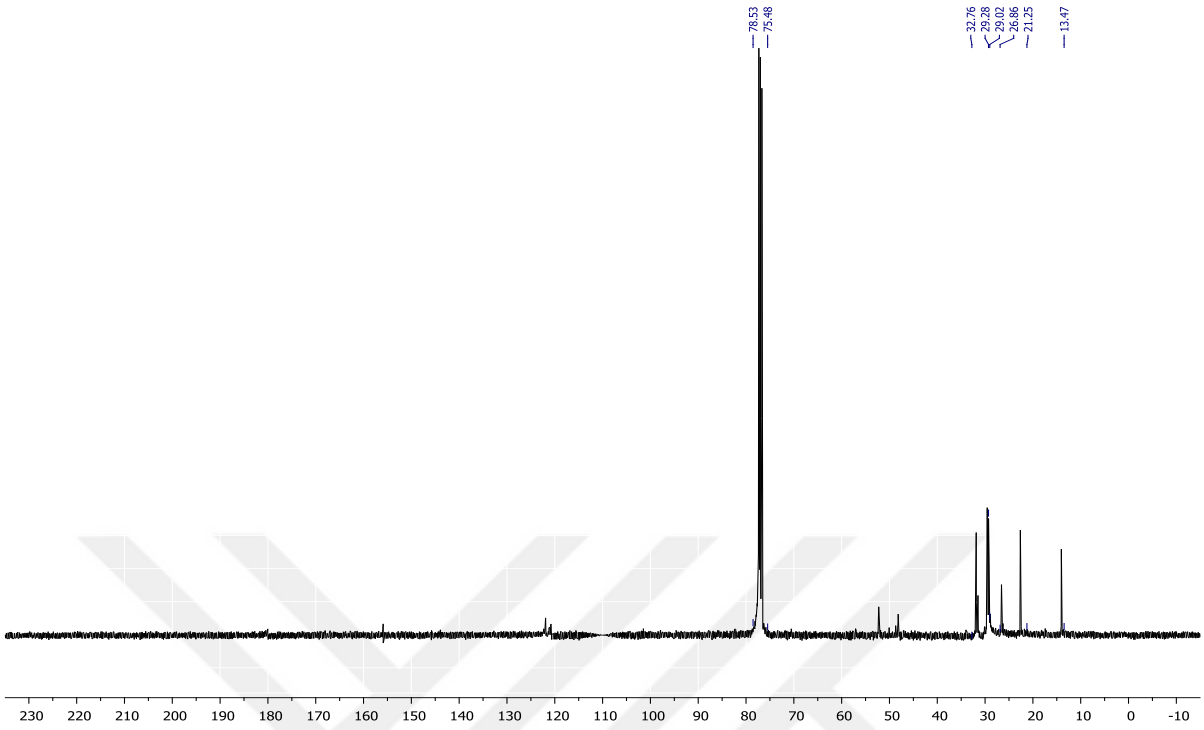
Appendice 31 The FT-IR Spectrum of 3c [1-octyl-3-(3-chloropropyl)-1H-imidazol-3-ium-2-yl]silver salt.

32.



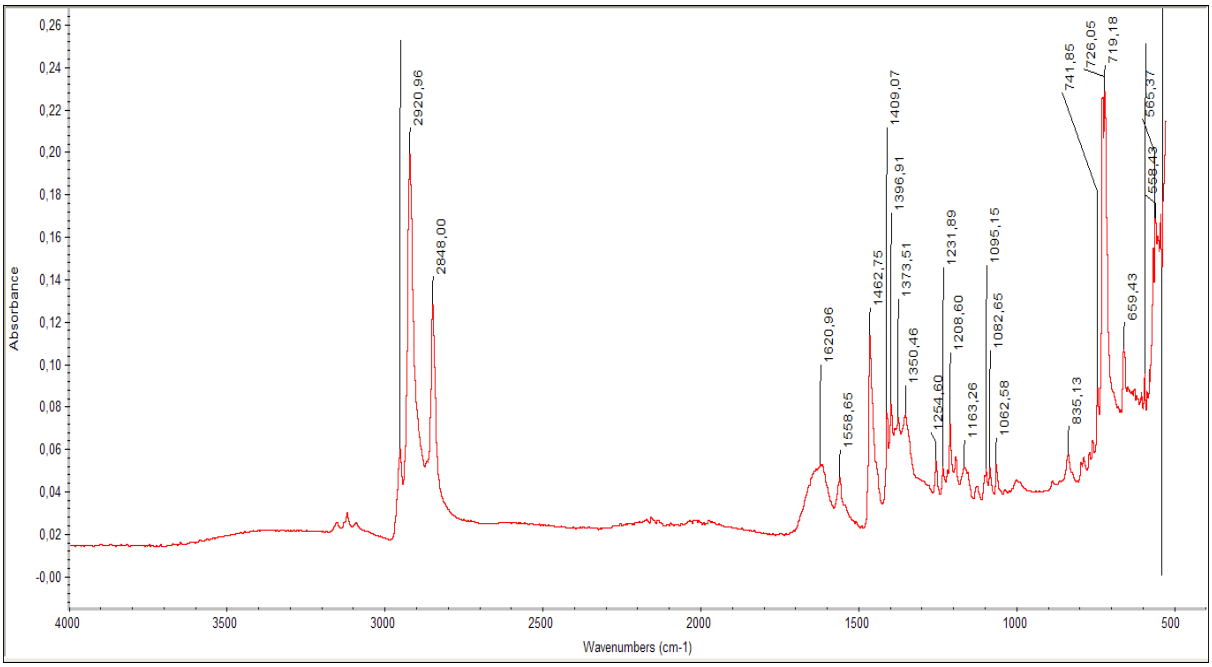
Appendice 32 The H^1NMR Spectrum of 3d [1-dodecly -3-(3-chloropropyl)-1H-imidazol-3-ium-2-yl]silver salt.

33.



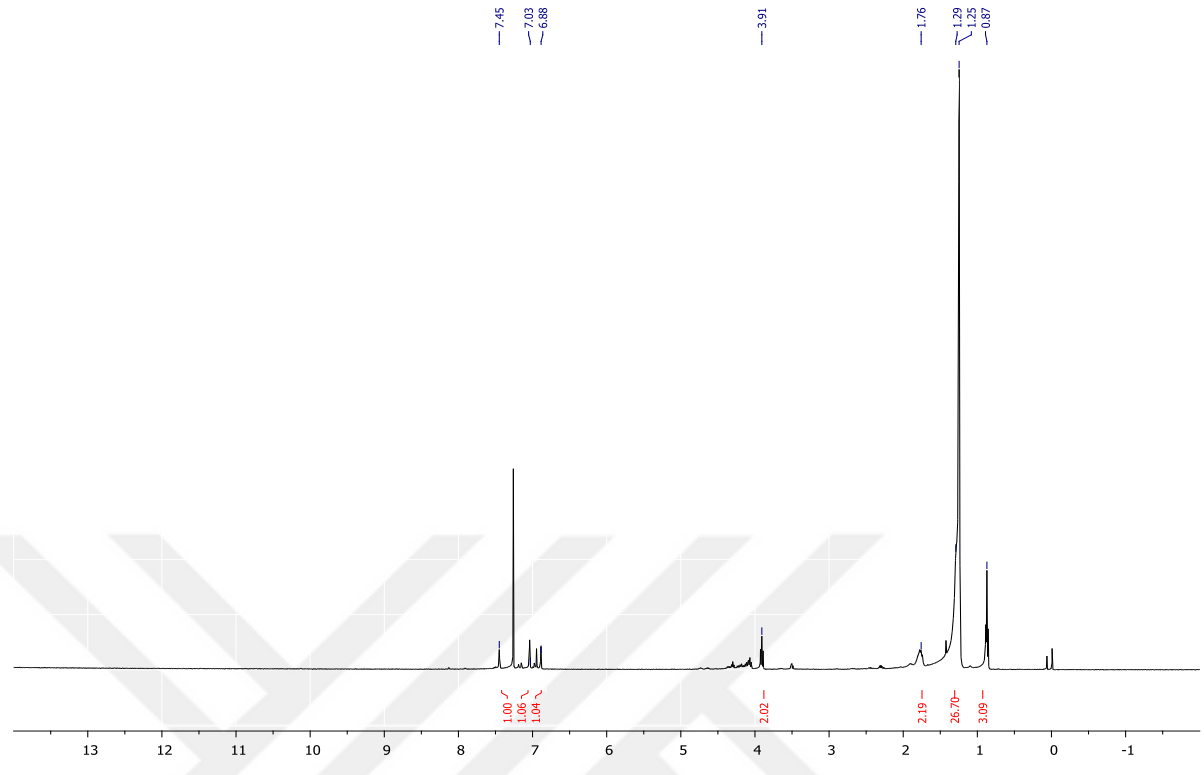
Appendice 33 The C^{13}NMR Spectrum of 3d [1-dodecyl-3-(3-chloropropyl)-1H-imidazol-3-ium-2-yl]silver salt.

34.



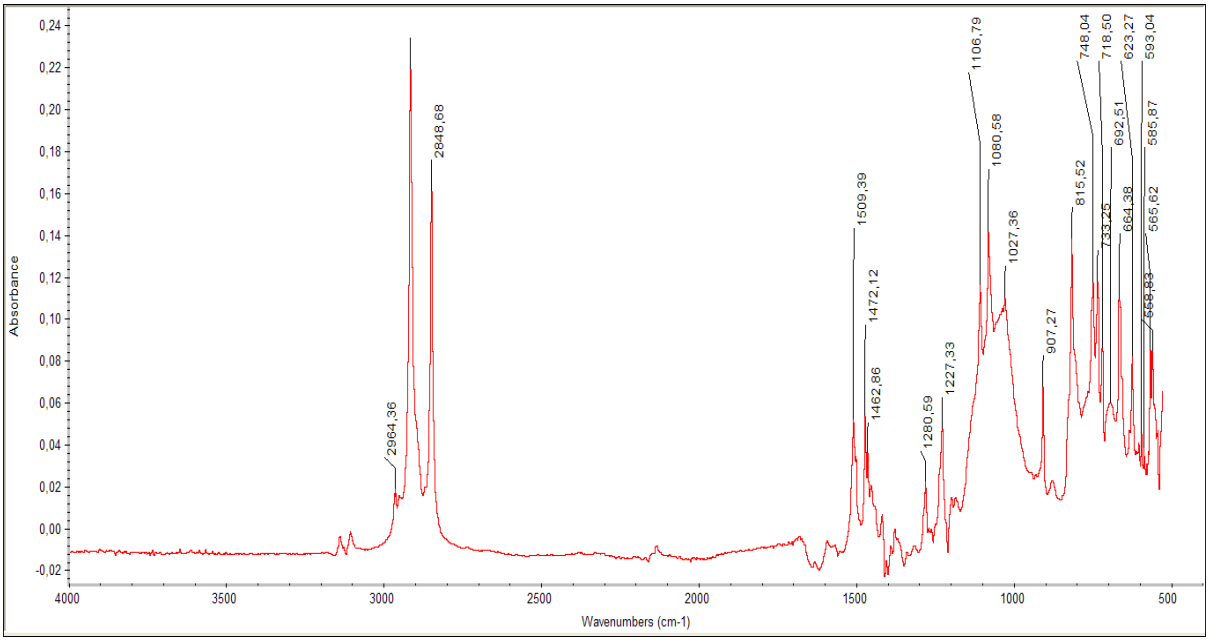
Appendice 34 The FT-IR Spectrum of 3d [1-dodecyl-3-(3-chloropropyl)-1H-imidazol-3-ium-2-yl]silver salt.

35.



Appendice 35 The H^1NMR Spectrum of 3e [1-hexadecyl-3-(3-chloropropyl)-1H-imidazol-3-ium-2-yl]silver salt.

36.



Appendice 36 The FT-IR Spectrum of 3e [1-hexadecyl-3-(3-chloropropyl)-1H-imidazol-3-ium-2-yl]silver salt.

REFERENCES

1. **Afşar, B.** Tekstil Sektör Analizi, 2007.
2. **İlter, M.** Tekstil Üretimi ve Yardımcı Kimyasallar, 2015.
3. www.ihkib.org.tr
4. **Palamutcu, Sema, et al.** "Fonksiyonel Tekstiller II: Antimikrobiyal Tekstiller." *Tekstil Teknolojileri Elektronik Dergisi*, 2009. **3**(3): p. 95-108.
5. **Gao, Yuan,** and **Robin Cranston**. "Recent advances in antimicrobial treatments of textiles." *Textile research journal*, 2008. **78**(1): p. 60-72
6. Lindemann B., Durable Antimicrobial Effects on Textiles, Melliand, 2000; 10:E205.
7. **Seong, H.S., Kim, J.P,** and **Ko, S.W** "Preparing chito-oligosaccharides as antimicrobial agents for cotton." *Textile Research Journal*, 1999. **69**(7): p. 483-488.
8. **Üreyen, M.E., et al**. "Yeni Geliştirilen Gümüş Katkılı Antimiktobiyal Tekstil Kimyasalı ve Bu Kimyasal İle İşlem Görmüş Kumaşların Antibakteriyel Performansları, *2008. (Cilt: 15)* p. 69.
9. **Menezes E.,** Özel Tekstiller için Antimikrobiyal Bitim İşlemi, International Dyer, 2002. December:13-16.
10. http://www.gemsan.com/bulten34.pdf
11. **Schmidt, M.** Dezenfeksiyon ve Sterilizasyon. In: Serter D.(ed), Nms-Mikrobiyoloji ve Enfeksiyon Hastalıkları. 3.Baskı, İstanbul: Nobel Tıp Kitabevleri Ltd Şti, 1997:61-3
12. **Kayser, F.H.,** Tıbbi Mikrobiyolojinin Temelleri. In: Anğ M. (ed), Tıbbi Mikrobiyoloji. 9.Baskı, İstanbul: Nobel Tıp Kitabevleri Ltd Şti, 2002:23-159.
13. **Hart, T.** and **Shears P.** Mikrobiyolojinin Kapsamı ve Mikroskopik İnceleme. In: Anğ Ö. (ed), Tıp Mikrobiyolojisi, İstanbul: Nobel Tıp Kitabevleri Ltd Şti, 2001; 1-79
14. http://www.tdctrade.com/imn/imnl7.
15. **Studer H.** Poliolefin Liflerinin Antimikrobik Korunması, Melliand Türkiye Sayısı, 1999; 1.
16. www.microlife.com/sw3291.asp.
17. **Seventekin, N., Öktem, T., Tekeoğlu, Ş.,** Tekstilde Antimikrobiyal Madde Kullanımı, Tekstil ve Konfeksiyon, sayı: 4, 2001, 217-224.
18. **Süpüren, G., Çay, A., Kanat, Z.E.,** and **Tarakçıoğlu, I**". Antimicrobial Fibers."*Tekstil ve Konfeksiyon Dergisi*, 2006. p. 80-89.
19. http://www.turkeyistanbul.com/html/modules.php?name=News&file=print&sid=247
20. MECİT, T. Y. M. D., Merkezi, T. T. A., ILGAZ, T. M. S., DURAN, A. G. D., GÜLÜMSER, T., & TARAKÇIOĞLU, I. (2007). TEKNİK TEKSTİLLER VE KULLANIM ALANLARI (BÖLÜM 2).
21. **Başer İ**. Tıpta Kullanılan Tekstil Materyalleri, Tekstil Teknik, 1995; 5:100.
22. **Studer H.** Poliolefin Liflerinin Antimikrobik Korunması, Melliand Türkiye Sayısı, 1999; 1.

23. **Saravanamuthu, R., Dubey, R.C,** and **Maheshwari, D.K.** Industrial Exploitation of Microorganisms. 'Biotechnological application in textile industry- antimicrobial textile ' R.RAJENDRAN Chapter 8 p.129-165
24. **Akaydın, M.,** and **Kalkancı, M.** "Hastane Giysisi Olarak Kullanılan Kumaşların Antibakteriyel Özellikleri Üzerine Bir Araştırma." *SDÜ Fen Dergisi*, 2014. **9**(1).
25. **Zikeli, S.** "Sea Cell® Active–A new cellulosic fiber with antimicrobial properties." *Avantex–International Forum and Symposium for High-Tech Apparel Textiles, Frankfurt/Main*. 2002.
26. **Seong, H. S., Kim, J. P.,** and **Ko, S. W.** Preparing chito-oligosaccharides as antimicrobial agents for cotton. *Textile Research Journal*,1999. ***69***(7): p. 483-488.
27. **Leonas, K. K.** And **Jinkins, R. S**. "The relationship of selected fabric characteristics and the barrier effectiveness of surgical gown fabrics. " *American journal of infection control*, 1997. **25**(1): p. 16-23.
28. **Bagherzadeh, R., et al.** "Evaluation of comfort properties of polyester knitted spacer fabrics finished with water repellent and antimicrobial agents." *Fibers and Polymers* 8.4 (2007): 386-392. , J. V. Edwards, T. Vigo, Bioact. Fibers&polymers, Am. Chem. Soc. Washington, DC, 2001
29. **Studer, H**. "Antimicrobial protection for polyolefine fibers." *Chemical Fibers International, 1997*. **47**(5): p. 373-373.
30. **Dastjerdi, R.** and **Majid M.** "A review on the application of inorganic nano-structured materials in the modification of textiles: focus on anti-microbial properties." *Colloids and Surfaces B: Biointerfaces*, 2010. **79**(1): p. 5-18.
31. **C. Can, A. Körlü,** Tekstil Teknolojileri Elektronik Dergisi, **2011**, 5, (54-59); Can, C., Körlü A.,13. Tekstil Teknolojisi ve Kimyasındaki Son Gelişmeler Sempozyum Kitabı, 171-174.
32. **C. K. Bower, J. E. Parker, A. Z. Higgins, M. E. Oest, J. T. Wilson, B. A. Valentine, M. K. Bothwell ve J. McGuire,** Colloids and Surfaces B: Biointerfaces, **2002**, 25, 81-90,.; B. Li, B. E. Logan, *Colloids and Surfaces B: Biointerfaces*, **2004**, 36, 81-90, Y. Z. Changa, W. B. Chu, Y. X. Sheng, W. Qiang, R. Liang, *Colloids and Surfaces B: Biointerfaces*, **2005,** 41, 79-81,
33. **X. H. Ren, L. Kou, H. B. Kocer, C. Y. Zhu,, S. D. Worley, R. M. Broughton, T. S. Huang,** Colloids and Surfaces A: Physicochem. Eng. Aspects, 345, 202-210, 2009; R. Dastjerdi, M. R. M. Mojtahedi, A. M. Shoshtari, A. Khosroshahi, *J. Textile Inst.*, 2010, 101, 204-213,
34. **Y. Hasebe, K. Kuwahara, S. Tokunaga,** AATCC-Review, 1, 23-28, 2001; Y. Kobayashi, T. Nakanishi, J. Komiyama, *Text. Res. J.*, **2002** 72, 125-131,
35. **R. Bagherzadeh, M. Montazer, M. Latifi, M. Sheikhzadeh, M. Sattari,** Fibers and Polymers, 2007, 8, 386-392, J. V. Edwards, T. Vigo, Bioact. Fibers&polymers, Am. Chem. Soc. Washington, DC, 2001
36. **Studer, H**. "Antimicrobial protection for polyolefine fibers." *Chemical Fibers International, 1997*. **47**(5): p. 373-373.
37. **V.A. Dorugade, K.** Bhagyashri Man-Made Text. India 53(3) (2010) 89
38. **A.J. Isquith, E.A. Abbott, P.A.** Walters Appl. Microbiol. 24(6) (1972) 859.
39. **Vigo, T. L.** "Protection of textiles from biological attack." *Handbook of fiber science and technology* 2 (1983): 367-427.
40. **Palamutcu, Sema, Et Al**. "Tekstil Ürünlerinde Antimikrobiyal Etkinlik Belirleme Testleri."

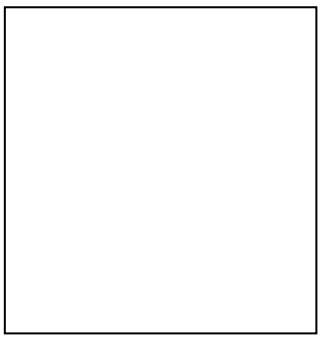
41. **Arslan, P.** and **Tayyar, A. E.** Tekstil Alanında Kullanılan Antimikrobiyal Maddeler, Çalışma Mekanizmaları, Uygulamaları ve Antimikrobiyal Etkinlik Değerlendirme Yöntemleri. *Düzce Üniversitesi Bilim ve Teknoloji Dergisi*, 2016. **4**(3).
42. **Gao, Y.** and **Cranston, R.** "Recent advances in antimicrobial treatments of textiles." *Textile research journal, 2008.* **78**(1): p.60-72.
43. **Wallace, M. L.,** Testing the Efficacy of Polyhexamethylene Biguanide as an Antimicrobial Treatment for Cotton Fabric, AATCC Review, 1, 18–20 (2001).
44. **Askew, P. D.** Analysis and assessment of current protocols to develop harmonised test methods and relevant performance standards for the efficacy testing of treated **articles/treated materials. ENV/JM/MONO, 2007.**
45. **Siu, Ralph Gun Hoy.** "Microbial decomposition of cellulose." *Microbial decomposition of cellulose.* (1951).
46. **Schindler, Wolfgang D., and Peter J. Hauser.** *Chemical finishing of textiles*. Elsevier, 2004.
47. **YAVUZ, MERVE.** INVESTIGATION OF OCCURENCE AND FATE OF BIOCIDES IN WASTEWATER TREATMENT PLANTS AND SURFACE WATERS. Diss. MIDDLE EAST TECHNICAL UNIVERSITY, 2013.
48. **Egger, Salome, et al**. "Antimicrobial properties of a novel silver-silica nanocomposite material." *Applied and environmental microbiology* 75.9 (2009): 2973-2976.
49. **Elsner, Peter.** "Antimicrobials and the skin physiological and pathological flora." *Biofunctional Textiles and the Skin*. Vol. 33. Karger Publishers, 2006. 35-41.
50. **Fouda, M. M. (2012).** *Antibacterial Modification of Textiles Using Nanotechnology* (pp. 47-72). INTECH Open Access Publisher.
51. **ÖZYURT, Mustafa.** "Aldehid, Peroksijen ve Perasetik Asit ile Klor Verici Ajan İçermeyen ve Alet Dezenfektanı Olarak Önerilen Diğer Dezenfektanlar, Genel Kullanım Alanları ve Antimikrobiyal Etkinlikleri." (2005).
52. **Jahangiri, Elham, et al.** "Laccase-and electrochemically mediated conversion of triclosan: Metabolite formation and influence on antibacterial activity." *Chemosphere* 168 (2017): 549-558.
53. **Kamalipour, Jamshid, et al**. "Preparation and release study of Triclosan in polyethylene/Triclosan anti-bacterial blend." *Colloids and Surfaces B: Biointerfaces* 145 (2016): 891-898.
54. **Singer, Heinz, et al**. "Triclosan: occurrence and fate of a widely used biocide in the aquatic environment: field measurements in wastewater treatment plants, surface waters, and lake sediments." *Environmental Science & Technology* 36.23 (2002): 4998-5004.
55. **Bostan, Kamil, T. Aldemir, and A. Aydın.** "Kitosan ve antimikrobiyal aktivitesi." *Türk Mikrobiyal Cem Dergisi* 37.2 (2007): 118-127.
56. **Dutta, P. K., et al.** "Perspectives for chitosan based antimicrobial films in food applications." *Food chemistry* 114.4 (2009): 1173-1182.
57. **Demir, Aslı, and Necdet Seventekin.** "Kitin, kitosan ve genel kullanım alanları." *Tekstil Teknolojileri Elektronik Dergisi* 3.2 (2009): 92-103.
58. **Kong, Ming, et al.** "Antimicrobial properties of chitosan and mode of action: a state of the art review." *International journal of food microbiology* 144.1 (2010): 51-63.

59. **Çay, A. , Duran, K.,** Chitosanın Tekstilde Kullanım Olanakları, Tekstil ve Konfeksiyon, sayı 1, 2004, 25-27
60. **Olcay, Hilal.** "KITIN VE KITOSANIN TEKSTIL VE BIYOMÜHENDISLIKTE UYGULAMALARI/BIOENGINEERING APPLICATIONS OF CHITIN AND CHITOSAN." *Istanbul Ticaret Universitesi Fen Bilimleri Dergisi* 14.28 (2015): 63.
61. **Seventekin, N., T. Öktem, and A. Korkmaz**. "Chitin ve Chitosan'ın Tekstil Sanayiinde Kullanım Olanakları." *Tekstil Terbiye ve Teknik, Sayı: Ağustos* (1999): 50-58.
62. **Lim, Sang-Hoon.** "Synthesis of a fiber-reactive chitosan derivative and its application to cotton fabric as an antimicrobial finish and a dyeing-improving agent." (2003).
63. **Fouda, Moustafa Mohamed Gaballa El-Sayed**. *Use of natural polysaccharides in medical textile applications*. Diss. Universität Duisburg-Essen, Fakultät für Chemie, 2005.
64. **Montazer, Majid, and M. Gorbanali Afjeh**. "Simultaneous x- linking and antimicrobial finishing of cotton fabric." *Journal of Applied Polymer Science* 103.1 (2007): 178-185.
65. **Timofeeva, Larisa, and Natalia Kleshcheva**. "Antimicrobial polymers: mechanism of action, factors of activity, and applications." *Applied microbiology and biotechnology* 89.3 (2011): 475-492.
66. **Ren, X., Kocer, H. B., Worley, S. D., Broughton, R. M., & Huang, T. S. (2009).** Rechargeable biocidal cellulose: Synthesis and application of 3-(2, 3-dihydroxypropyl)-5, 5-dimethylimidazolidine-2, 4-dione. *Carbohydrate Polymers*, *75*(4), 683-687.
67. **Maddah, Bozorgmehr.** "Anti-bacterial Activity of N-halamin in Hospital Fabrics: New Synthesis Approach and Examination of Anti-Bacterial Characteristics." *J Life Sci Biomed* 4.6 (2014): 575-578.
68. **Huang, Louise K., and SUN GANG. "**Durable and regenerable antimicrobial cellulose with oxygen bleach: concept proofing." *AATCC review* 3.10 (2003): 17-21.
69. **Huang, Louise K., and Gang Sun**. "Durable and oxygen bleach rechargeable antimicrobial cellulose: sodium perborate as an activating and recharging agent." *Industrial & engineering chemistry research* 42.22 (2003): 5417-5422.
70. **Sun, Gang, and Louise Ko Huang**. "Regenerable antimicrobial polymers and fibers with oxygen bleaches." U.S. Patent No. 6,962,608. 8 Nov. 2005.
71. **Sun, Gang, and Louise Ko Huang.** "Regenerable antimicrobial polymers and fibers with oxygen bleaches." U.S. Patent No. 6,962,608. 8 Nov. 2005.
72. **Simoncic, Barbara, and Brigita Tomsic.** "Structures of novel antimicrobial agents for textiles-a review." *Textile Research Journal* 80.16 (2010): 1721-1737.
73. **Blackburn, Richard S., et al.** "Sorption of poly (hexamethylenebiguanide) on cellulose: mechanism of binding and molecular recognition." *Langmuir* 22.13 (2006): 5636-5644.
74. **Chadeau, Elise, et al.** "EVALUATION OF ANTIMICROBIAL ACTIVITY OF A POLYHEXAMETHYLENE BIGUANIDE- COATED TEXTILE BY MONITORING BOTH BACTERIAL GROWTH (ISO 20743/2005 STANDARD) AND VIABILITY (LIVE/DEAD BACLIGHT KIT)." *Journal of Food Safety* 32.2 (2012): 141-151.

75. **Rai, M., Yadav, A., & Gade, A. (2009).** Silver nanoparticles as a new generation of antimicrobials. *Biotechnology advances*, *27*(1), 76-83.
76. Hipler, U.C. and Elser, P. Biofunctional Textiles and the Skin, Current problems in dermatology, 2006. v. 33 p. 116.
77. **Hill, W. R., & Pillsbury, D. M. (1939).** *Argyria: the pharmacology of silver*. Williams & Wilkins Company.
78. **Alexander, J. W. (2009).** History of the medical use of silver. *Surgical infections*, *10*(3), 289-292.
79. **Sims MJ.** The Story of My Life. Marion-Sims H, ed. New York. D. Appleton & Co., 1884.
80. **Schneider, G. E. R. D. (1984).** Silver nitrate prophylaxis. *Canadian Medical Association Journal*, *131*(3), 193.
81. **Li, W. R., Xie, X. B., Shi, Q. S., Zeng, H. Y., You-Sheng, O. Y., & Chen, Y. B.** (2010). Antibacterial activity and mechanism of silver nanoparticles on Escherichia coli. *Applied microbiology and biotechnology*, *85*(4), 1115-1122.
82. **Feng, Q. L., Wu, J., Chen, G. Q., Cui, F. Z., Kim, T. N., & Kim, J. O.** (2000). A mechanistic study of the antibacterial effect of silver ions on Escherichia coli and Staphylococcus aureus. *Journal of biomedical materials research*, *52*(4), 662-668.
83. **Holt, K. B., & Bard, A. J.** (2005). Interaction of silver (I) ions with the respiratory chain of Escherichia coli: an electrochemical and scanning electrochemical microscopy study of the antimicrobial mechanism of micromolar Ag+. *Biochemistry*, *44*(39), 13214-13223.
84. **Jeong, S. H., Yeo, S. Y., & Yi, S. C.** (2005). The effect of filler particle size on the antibacterial properties of compounded polymer/silver fibers. *Journal of Materials Science*, *40*(20), 5407-5411.
85. **Yeo, S. Y., Lee, H. J., & Jeong, S. H.** (2003). Preparation of nanocomposite fibers for permanent antibacterial effect. *Journal of Materials Science*, *38*(10), 2143-2147
86. **Kascatan-Nebioglu, A., Melaiye, A., Hindi, K., Durmus, S., Panzner, M. J., Hogue, L. A., ... & Milsted,** A. (2006). Synthesis from caffeine of a mixed N-heterocyclic carbene− silver acetate complex active against resistant respiratory pathogens. *Journal of medicinal chemistry*, *49*(23), 6811-6818.
87. **Özdemir, İ., Demir, S., Günal, S., Özdemir, İ., Arıcı, C., & Ülkü, D.** (2010). Synthesis, characterization and antimicrobial activity of new silver complexes with N-heterocyclic carbene ligands. *Inorganica Chimica Acta*, *363*(14), 3803-3808.
88. **Butorac, R. R., Al-Deyab, S. S., & Cowley, A. H.** (2011). Antimicrobial properties of some bis (iminoacenaphthene (BIAN)-supported N-heterocyclic carbene complexes of silver and gold. *Molecules*, *16*(3), 2285-2292.
89. Siciliano T.J., Deblock M. C., Hindi K. M., Durmuş S., Panzner M. J., Tessier C. A. and Youngs W. J., *J. Organometallic Chem.*, 2011, 1066-1071,
90. **Kou, L., Liang, J., Ren, X., Kocer, H. B., Worley, S. D., Tzou, Y. M., & Huang, T. S.** (2009). Synthesis of a water-soluble siloxane copolymer and its application for antimicrobial coatings. *Industrial & Engineering Chemistry Research*, *48*(14), 6521-6526.
91. **Kalyon BD, Olgun U**: Antibacterial efficacy of triclosan-incorporated polymers. Am J Infect Control 2001;29:124–125.

92. **Damm, C., & Münstedt, H.** (2008). Kinetic aspects of the silver ion release from antimicrobial polyamide/silver nanocomposites. *Applied Physics A*, *91*(3), 479-486.
93. **Liebner, F., Patel, I., Ebner, G., Becker, E., Horix, M., Potthast, A., & Rosenau, T.** (2010). Thermal aging of 1-alkyl-3-methylimidazolium ionic liquids and its effect on dissolved cellulose. *Holzforschung*, *64*(2), 161-166.
94. **El Seoud, O. A., Pires, P. A. R., Abdel-Moghny, T., & Bastos, E. L.** (2007). Synthesis and micellar properties of surface-active ionic liquids: 1-alkyl-3-methylimidazolium chlorides. *Journal of colloid and interface science*, *313*(1), 296-304.

CURRICULUM VITAE



Name Surname : Nurgül MUTLU

Place and Date of Birth : KIRCAALI / 06.02.1991

E-Mail: nurgul.mutlu@outlook.com

EDUCATION:

- B.Sc. : 2013, Ege University, Faculty of Scienc, Chemistry

PUBLICATIONS, PRESENTATIONS AND PATENTS ON THE THESIS:

Nurgül Mutlu, Candan AKCA, İlknur Özdemir, Selami Günal, Zeynep Taşcı, The Investigation of Antibacterial and Antifungal Efficiencies of the Textile Immobilized Ag-NHC (N-Heterocyclic carbene) Complexes, *The First International Conference on Green Chemistry and Sustainable Technologies* 21-23 Ekim 2015, Çeşme, Turkey.