

COURSE GUIDE

CHM 312 INDUSTRIAL CHEMICAL PROCESSES

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INTRODUCTION

Welcome to CHM 312: Industrial Chemical Processes I, which is a two credit unit course, offered in the third year to students of the undergraduate degree programme in Chemistry. There are twelve study units in this course. This course guide is designed for distance learners enrolled in the BSc. Chemistry programme of the National Open University of Nigeria. This guide is one of the several resource tools available to you to help you successfully complete this course and ultimately your programme.

In this guide, you will find very useful information about this course such as aims, objectives, available services to support your learning, information on assignments and examination, guidelines on time management for the study, and tutor-marked assignments. When working through this course, ensure you minimize distractions and be prepared to focus on the course material. The more time you put into the course, the more you will receive from it. Take and record your notes on the printed materials so that you can make connections between the topics. There is no reason to be confused or frustrated. The i-learn platform will enable you to reach out to your fellow students, the course facilitator and instructor through the discussion board.

In this course, you will be introduced to a wider application of the fermentation process in industries and the processes involved in the manufacture of wine and beer. You will also learn how monomers are linked together covalently in a chemical process known as polymerization. You will also be exposed to the processes involved in manufacturing Polyethylene and Styrene Butadiene Rubber (SBR). In addition, you will learn how pharmaceuticals such as penicillin and aspirin are manufactured. This course will also introduce you to the Pesticide Industry, the various ways of classifying pesticides as well as examples of pesticides and their manufacturing processes. You will also learn about the dyes industry, the classification of dyes and the manufacturing process of dyes. You will also learn about compounds that are used as flavoring agents and the processes involved in their manufacture. Finally, this course will enlighten you on the various types of explosives and adhesives and their manufacturing processes.

I wish you all the best in your learning experience and successful completion of this course.

COURSE DESCRIPTION

Industrial chemical processes I (CHM 312) covers the production of primary intermediates and synthesis of industrial organic chemicals

such as polymers, adhesives, dyes, explosives, insecticides, pesticides, herbicides, flavoring agents, pharmaceuticals and fermentation process.

COURSE AIMS

The course aims to improve the knowledge of learners on synthesis of industrial chemicals with emphasis on recent technological development. You will be exposed to the production trends in various chemical industries.

COURSE OBJECTIVES

There are objectives to be achieved in each study unit of the course. You should read them before studying each unit. On completion of the course, you should be able to:

- Describe the fermentation processes of wine and beer.
- Classify polymers and describe the manufacturing process of a named polymer.
- Explain how penicillin and aspirin are manufactured
- Identify chemical reactions involved in production of pesticides
- Describe the production processes of some important pesticides
- Classify dyes based on at least four criteria.
- Describe the manufacturing process of dyes.
- Give some examples of flavoring agents and explain how they are produced.
- Explain the processes employed in handling fruit flavours.
- Classify explosives and explain with specific examples.
- Explain the manufacturing processes of various adhesives.

WORKING THROUGH THIS COURSE

In order to be able to successfully complete this course, you should carefully study each unit in details along with the recommended further readings. Also, you need to ensure that you plan your study time. To get the best from this course, ensure you make notes of key points at the margin which can be later used for revision purpose. Each unit contains self-assessment exercise and at certain points in the course you would be required to submit assignment for grading and recording purposes. You are also to participate in the final examination at the end of the course. Ensure you give quality time to reading and comprehension. It is crucial that you attempt the tutor-marked assignments and participate in online facilitation and group discussion via the i-learn platform.

COURSE MATERIAL AND STRUCTURE

The course material is divided into three modules which are further subdivided into study units. The course is made up of two components:

- Course guide
- Study Units

The following are the three modules and twelve units contained in this course:

Module 1

Unit 1	Fermentation
Unit 2	Manufacturing Process of Beer
Unit 3	Manufacturing Process of Wine
Unit 4	Pharmaceutical

Module 2

Unit 1	Polymers
Unit 2	Polyethylene
Unit 3	Styrene Butadiene Rubber

Module 3

Unit 1	Pesticides
Unit 2	Dyes
Unit 3	Flavouring agents
Unit 4	Explosives
Unit 5	Adhesives

ASSESSMENT

The course assessment consists of three aspects; namely, the self-assessment exercise, the tutor-marked assignment and the end-of-course examination. It is essential that you attempt all exercises and assignments. Let your answers be concise and as accurate as possible. You are expected to consult other materials in addition to your course materials in order to be able to present accurate answers to the questions. Please note that the tutor-marked assignment covers only 30% of the total score obtainable for the course.

TUTOR-MARKED ASSIGNMENT (TMA)

The TMA is a continuous assessment component of your course. The assignments are designed to cover all areas treated in the course. You will be required to attempt four TMAs as part of the requirement for the completion of this course. You will be assessed on all four, but the best three performances will be used for your continuous assessment. Each assignment carries 10% and together will account for 30% of your total score for the course. The assignments must be submitted on or before the stipulated dates for submission. You may do yourself good by reading and researching well before you attempt to answer the questions.

FINAL EXAMINATION AND GRADING

The final examination of CHM 312 will carry 70% of the total course grade. The duration of the exam will be two hours. The examination will consist of questions which reflect the kind of tutor-marked assignments which you have previously encountered. All areas of the course will be assessed. You should use the time between completion of the course content and beginning of the examination to revise the entire course and the assignments given. The end-of-the-course examination is intended to cover information from all parts of the course. The final examination accounts for 70% of the total score for this course. To be eligible to sit for the examination, you should have submitted the four tutor-marked assignments and registered to sit for the examination.

CONCLUSION

All the features of this course guide have been designed to facilitate your learning so as to comfortably achieve the aims and objectives of the course. You should ensure that you make maximum use of them in your study in order to achieve maximum result.

MAIN COURSE

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MODULE 1

Unit 1 Fermentation

3.3 Fermentation Process of Wine

https://www.youtube.com/watch?v=W2X_5GPxEFE

3.3.3 Fermentation

Alcoholic Fermentation

<https://www.youtube.com/watch?v=jOMO8pIrZEw>

Lactic Acid Fermentation

<https://www.youtube.com/watch?v=wcwq1aBNpgY>

UNIT 1 FERMENTATION

CONTENTS

- 1.0 Introduction
- 2.0 Objectives
- 3.0 Main Content
 - 3.1 History of Fermentation
 - 3.2 Classification of Fermentation
 - 3.2.1 Microbial Fermentation
 - 3.2.2 Enzymatic Fermentation
 - 3.3 Fermentation Process
 - 3.3.1 Culture Preservation
 - 3.3.2 Scale Up
 - 3.3.3 Fermentation
 - 3.4 Product Recovery and Purification
- 4.0 Self-Assessment Exercise
- 5.0 Conclusion
- 6.0 Summary
- 7.0 References/Further Reading

1.0 INTRODUCTION

In this unit, you will learn about the history and classification of fermentation. You will also learn about the three processes involved in fermentation. You will also be able to explain how a fermentation product can be recovered and purified.

2.0 OBJECTIVES

By the end of this unit, you should be able to:

- explain the term “fermentation”
- give a brief history of fermentation.
- give the names of three scientists that made significant contribution to the concept of fermentation.
- explain the two major classes of fermentation.
- describe the three processes in fermentation.
- list the unit operations involved in a fermentation product recovery and purification.

3.0 MAIN CONTENT

3.1 History of fermentation

Fermentation is a natural process. People applied fermentation to make products such as wine, cheese and beer long before the scientific nature of the process was understood. This nature was first explored by Louis Pasteur, a French chemist who considered fermentation as a life process. According to him, all fermentative changes are associated with and produced by living organisms. Justus von Liebig, a German chemist, on the other hand, considered it to be a simple chemical process brought about by complex nitrogenous substances, already present in the cells of microorganisms. The controversy between Pasteur and Liebig over the nature of alcoholic fermentation was uncovered by Eduard Buchner, a German chemist and zymologist. His findings revealed that fermentation could occur in the presence of oxygen and was caused by an enzyme which he named zymase. The simple most common meaning of fermentation is the conversion of a sugar into an organic acid or an alcohol. Fermentation occurs naturally in many foods and humans intentionally used it since ancient times to improve both the preservation and organoleptic properties of food.

3.2 Classification of fermentation

Fermentation is a process by which a raw material is converted into a product by the action of micro-organisms or by means of enzymes. The two major classes of industrial fermentation are:

3.2.1 Microbial fermentation

These are promoted by micro-organisms such as bacteria, viruses, fungi and protozoans. During microbial fermentation, the rate of conversion of raw materials to products is at first low because the micro-organisms (which serve as the catalytic agent) are few. As more micro-organisms are formed, the rate starts to rise. The rate then reaches a maximum when there is optimum ratio of unconverted material to the micro-organisms. The rate then drops as the raw material becomes depleted. Finally, the rate stops when the raw material is finished. Micro-organisms are able to catalyze many types of reactions. As a result, microbial fermentation results in more than one product which makes purification essential.

3.2.2 Enzymatic fermentation.

These are catalyzed by enzymes. Enzymes are natural proteins which act as biocatalysts that bring about specific biochemical reactions without their structure or quantity being changed. Their activity depends on temperature, pH; storage time and storage conditions. Because enzymes are specific in action, only one product is produced from a selected enzyme and therefore, its purification is less expensive compared to microbial fermentation. However, enzymes are more expensive than micro-organisms.

3.3 Fermentation Process.

The fermentation process involves the following:

3.3.1 Culture Preservation

For any fermentation process to be successful, a preserved high yielding micro-organism strain is a basic necessity. The preserved culture is a valuable asset and as little as possible should be used to initiate the process. Generally, this preserved stock is in the form of inert spores.

3.3.2 Scale Up

Scale up is an important part of many cell driven processes. For some fermentation, it is essential to amplify the starting inoculum through a series of ever increasing volumes until enough material exists to inoculate the production system. In bacterial and yeast systems where vigorous growth is anticipated, scale up to an initial: final inoculum ratio of 1:20 to 1:100 is common.

The seed tanks are steel tanks designed to provide an ideal environment for growing microorganisms. They are filled with all the things the specific microorganism would need to survive and thrive,

including warm water and carbohydrate foods like lactose or glucose sugars. Additionally, they contain other necessary carbon sources, such as acetic acid, alcohols, or hydrocarbons, and nitrogen sources like ammonium salts. Growth factors like vitamins, amino acids, and minor nutrients complete the composition of the seed tank contents. The seed tanks are equipped with mixers, which keep the growth medium moving, and a pump to deliver sterilized, filtered air. After about 24-28 hours, the material in the seed tanks is transferred to the primary fermentation tanks.

3.3.3 Fermentation

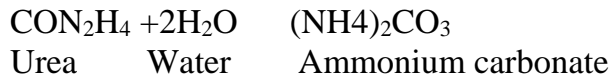
Essentially, the fermentation tank is a larger version of the seed tank. It is filled with the same growth media found in the seed tank and also provides an environment conducive for the growth and multiplication of the microorganisms.

During this process, they excrete large quantities of the desired product. The tanks are cooled to maintain the right temperature. The fermentation tank is constantly agitated, and a continuous stream of sterilized air is pumped into it. Anti-foaming agents are periodically added to inhibit foaming. Acids or bases are added to control pH to the level which is optimal for the growth of the microorganism.

The fermenter is the heart of any fermentation process. The design of fermentation equipment and the operation of the fermentation process must ensure the process is contamination free, and in the case of pathogens, they must be contained with high degree of safety. Most production fermenters are made of stainless steel construction with impellers for good bulk liquid mixing characteristics to ensure homogeneity within the vessel. Air is sparked into the vessel below the bottom impeller. Fermenters produce heat through dispersion of kinetic energy and metabolism, therefore the vessel must have a cooling system. An industrial microbiology fermentation usually refers to the production of chemical substances by use of microorganisms.

Alcoholic fermentation: the fermentation which saccharine bodies undergoes when brought in contact with the yeast plant or tonila. The sugar is converted either directly or indirectly into alcohol and carbonic acid, the rate of action being dependent on the rapidity with which the Tonilae develop

Ammoniacal Fermentation: the conversion of the urea of urine into ammonium carbonate through the growth of the special urea fermentation



When urine is exposed to the air in open vessels for several days, it undergoes this alkaline fermentation

Butyric Fermentation: The decomposition of various forms of organic matter through the agency of a peculiar worm-shaped vibrio with formation of more or less butyric acid. It is one of the many forms fermentation that collectively constitute putrefaction.

Glycerin Fermentation: Fermentation which occurs on mixing a dilute solution of glycerin with a peculiar species of schizomycetes and some carbonates of lime and other matter favorable to the growth of the plant, the glycerin being changed into butyric, caproic acid butyl, butyl and ethyl alcohol.

Lactic Fermentation: The transformation of milk sugar or other saccharine body into lactic acid as in the scouring of milk, through the agency of a special bacterium (*Bacterium lactis of lister*).

3.4 Product Recovery and Purification

Recovery and purification are very essential steps for a fermentation product to be economically attractive. Certain products are contained inside the cells and are not released or are only partially released to the medium. It may be necessary to wash the cells to remove impurities before breaking them to get the product.

Some cells have high resistance to shear and require specialized equipment to rupture them. Ultrasonic vibrations, grinding in mills and high pressure can be used to rupture cells. Centrifuges and rotary-drum filtering are commonly used in the separation of the cells from the broth. Products in the broth may be recovered by a variety of unit operations such as distillation, extraction with salts and solvents, membrane ultrafiltration, precipitation and chromatography.

SELF-ASSIGNMENT EXERCISE

- i. Mention three scientists that made contributions to the concept of fermentation.
- ii.
 - a. What is fermentation?
 - b. Explain the two major classes of industrial fermentation.
- iii. What are the unit operations involved in a fermentation product recovery and purification?

4.0 CONCLUSION

Several scientists made contributions to fermentation. Fermentation process can be carried out by either microorganisms or enzymes. Fermentation is carried out in three processes which are culture preservation, scale up and fermentation itself. Recovery and purification of fermentation product are essential in order for the product to be economically attractive. Some of the operations involved in recovery of products are distillation, extraction with salts and solvents etc.

5.0 SUMMARY

In this unit, you have learnt about the history of fermentation, the two major classes of fermentation, the fermentation process and recovery and purification of fermentation product. Edward Buchner findings revealed that fermentation could occur in the presence of oxygen and was caused by an enzyme which he named zymase. Fermentation is classified into microbial and enzymatic fermentation. Culture preservation and Scale up are the two types of fermentation process. The design of fermentation equipment and the operation of the fermentation process must ensure the process is contamination free, and in the case of pathogens, they must be contained with high degree of safety. An industrial microbiology fermentation usually refers to the production of chemical substances by use of microorganisms. Recovery and purification are very essential steps for a fermentation product to be economically attractive.

6.0 TUTOR-MARKED ASSIGNMENT

Divide the class into suitable groups, let each group describe how to produce alcohol using a named local agricultural produce

7.0 REFERENCES/FURTHER READING

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Voet, Donald & Voet, Judith G. (1995). *Biochemistry* (2nd ed.). New York, NY: John Wiley & Sons. ISBN 978-0-471-58651-7.

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Leona P, Petra P and Tomas B (2013) Advanced Fermentation Process

UNIT 2 MANUFACTURING PROCESS OF BEER

3.1 Manufacturing Process of Beer

<https://www.youtube.com/watch?v=TY2xTdlJQrg>

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- 1.0 Introduction
- 2.0 Objectives
- 3.0 Main Content
 - 3.1 Manufacturing Process of Beer
- 4.0 Conclusion
- 5.0 Summary
- 6.0 Tutor-Marked Assignment
- 7.0 References/Further Reading

1.0 INTRODUCTION

You are familiar with the old example of fermentation of sugars to alcohols and carbon dioxide by yeast. You will now be introduced to a wider application of fermentation. You will learn about the manufacturing process of beer.

2.0 OBJECTIVES

By the end of this unit, you should be able to:

- explain the brewing process.

3.0 MAIN CONTENT

3.1 Manufacturing Process of beer

The process of manufacturing beer is known as brewing. A key ingredient in this process is malted grain. The first step in brewing is known as malting. This involves steeping the grain in water for several days until it begins to germinate or sprout. The germination process creates a number of enzymes, notably alpha-amylase and beta-amylase, which will be used to convert the starch in the grain into sugar. At this point, the grain is called malt. After several days, when the majority of the starch has been converted to sugar, the malt is

heated and dried. This process, called kilning, stops the malt from germinating any further.

After kilning, the dried malt is crushed in a malt mill to break apart the grain kernels, increase their surface area and separate the smaller pieces from the husks. The cracked malt is transferred to a container called a mash tun, and hot water is added. During this process which is known as “mashing”, the malt steeps in the liquid, usually for one to two hours and natural enzymes within the malt break down the complex sugars in the grain, release them in the water and produce sweet liquid called wort. The final step is called brewing. The wort is transferred to a large brew kettle and boiled for up to two hours. Boiling effectively sterilizes the wort to kill any bacteria that may spoil the wort during fermentation. During this stage of the brewing process, hops are added to the wort to provide a spicy flavor, aroma and bitterness that balances the sweetness of the wort. The types of hops used and the length of time they are boiled are determined by the style of beer being made. To produce a beer with a stronger, bitterer flavor, hops are boiled for at least 30 minutes and often longer. This enables the bitter oils in the hops to fully infuse into the wort.

After brewing, the wort is cooled and then strained to remove the hop leaves and other residues. The wort is then transferred into a temperature controlled cylindrical-conical “fermenter”. Yeast is then added or *pitched* into the wort to begin fermentation. The yeast converts the sugars from the malt into alcohol, carbon dioxide and other components through a process called fermentation or glycolysis. The first fermentation lasts from a few days to two weeks. When the yeast has consumed most of the fermentable sugar, the wort becomes beer. The beer is transferred to an air tight container, called a conditioning tank, for a second fermentation or aging period, where the beer becomes naturally carbonated. Some brewers inject carbon dioxide gas into the beer when aging is complete to give it a bubbly, effervescent quality. Aging lasts for a few weeks to several months, depending on the type of beer being produced.

SELF-ASSIGNMENT EXERCISE

- i. Define brewing.
- ii. Describe in details the industrial process of manufacturing beer.

Brewing is known as malting and involves steeping the grain in water for several days until it begins to germinate or sprout. The germination process creates a number of enzymes, notably alpha-amylase and beta-amylase, which will be used to convert the starch in the grain into sugar. At this point, the grain is called malt. After several

days, when the majority of the starch has been converted to sugar, the malt is heated and dried. This process, called kilning, stops the malt from germinating any further. After kilning, the dried malt is crushed in a malt mill to break apart the grain kernels, increase their surface area and separate the smaller pieces from the husks. The cracked malt is transferred to a container called a mash tun, and hot water is added. This process is known as “mashing” and the malt steeps in the liquid for one to two hours and natural enzymes within the malt break down the complex sugars in the grain, release them in the water and produce sweet liquid called wort. The final step is called brewing. The wort is transferred to a large brew kettle and boiled for two hours, this sterilizes the wort to kill any bacteria that may spoil the wort during fermentation. During this stage of the brewing process, hops are added to the wort to provide a spicy flavor, aroma and bitterness that balances the sweetness of the wort.

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4.0 CONCLUSION

The steps involved in the manufacturing of beer are malting, kilning, mashing and brewing.

5.0 SUMMARY

In this unit, you have learnt in details the brewing process. Malting is the first stage which involve steeping the grain in water for several days until it begins to germinate or sprout. This is to create a number of enzymes, notably alpha-amylase and beta-amylase which is used to convert the starch in the grain into sugar. The next process is called kilning, heating and drying the malt after conversion of starch to sugar (mashing), followed by production of sweet liquid called wort and then brewing. The wort is transferred to a large brew kettle and boiled for up to two hours. Boiling effectively sterilizes the wort to kill any bacteria that may spoil the wort during fermentation. During this stage of the brewing process, hops are added to the wort to provide a spicy flavor, aroma and bitterness that balances the sweetness of the wort.

We shall now consider the manufacturing process of wine in the next unit.

6.0 TUTOR-MARKED ASSIGNMENT

List all the possible raw materials used in making beer that are available in Nigeria

7.0 REFERENCES/FURTHER READING

D.I.C. Wang, C.L. Cooney, A.L. Domain, P. Dunnill, A.E. Humphrey and M.D. Lilly (1979). Fermentation and Enzyme Technology, Vols 1,

http://www.sterkensbrew.be/sbm/beer_making.html

A. N Eboatu, E. N Ejike and V. N Okafor (2016) Evaluation of anti-nutritional factors in hop extract and

From Azadirachta indica as potential substitute in the Nigerian beer industry. Int. J. Appl. Sci. 2 (11):114

UNIT 3 MANUFACTURING PROCESS OF WINE

3.1 Manufacturing Process of Wine

<https://www.youtube.com/watch?v=FAIyzK9cqPY>

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- 5.0 Summary
- 6.0 Tutor-Marked Assignment
- 7.0 References/Further Reading

1.0 INTRODUCTION

You are familiar with the old example of fermentation of sugars to alcohols and carbon dioxide by yeast. You will now be introduced to wider application of fermentation. You will learn about the manufacture of wine.

2.0 OBJECTIVES

At the end of this unit, you should be able to explain the manufacturing process of wine.

3.0 MAIN CONTENT

3.1 Manufacturing Process of Wine

Oenology is the term that is used to describe the science of wine making. A person who makes wine is traditionally called a winemaker or vintner. Wines are prepared by the fermentation of fruit juices, most important of which is grape juice. The single most important factor that contributes to the character of wine is the grapes that are used. Grapes influence the flavour, colour, alcohol content and acidity of wine. White wine (straw to golden-yellow in color) is produced from white grapes while red wine is produced from red grapes. Red and white wine production is basically the same except for one primary difference: the presence of the grape skins during fermentation. White grapes are crushed and the juice separated from the skins prior to

fermentation. Red wine is fermented with the grape skins. The juice extracted from the grapes is called must.

The wine-making process can be divided into four distinct steps:

- Harvesting and crushing grapes
- Fermenting must
- Ageing the wine
- Packaging

The grapes are harvested from the vineyards and taken to a winery where they are passed through a machine called a destemmer crusher that separates the fruit from the stems and cracks the berries open to release the juice. To make white wine, the must is transferred to a press where pressure is applied to separate the juice from the skins. After pressing, the white juice without the skins is transported to a fermentation tank. In red wine production, the whole crushed grape, including the skin, goes into the fermentation tank (The pigment in the grape skins give red wine its color). The amount of time the skins are left in the tank determines how dark or light the color will be. During the fermentation process, wild yeast is fed into the tank to turn the sugar in the must into alcohol. To add strength, varying degrees of yeast may be added. The wine must ferment in the tank for approximately seven to fourteen days, depending on the type of wine being produced.

After fermentation, certain wines (mainly red wine) will be crushed again and pumped into another fermentation tank where the wine will ferment again for approximately three to seven days. This is done not only to extend the wine's shelf life but also to ensure clarity and color stability. When fermentation is complete, red wine is separated from the stems and grape skins by passing it through a press. Both red and white wines appear cloudy after fermentation, and the wine maker must wait for the yeast and other solids to settle to the bottom of the fermentation tank, forming sediment called the *lees*. The clear wine is *racked* or drawn off the lees and stored in a clean cask.

After crushing and fermentation, wine needs to be stored, filtered, and properly aged. Good sweet wine can be obtained by a quick ageing method in about four months. Pasteurization, refrigeration, sunlight, ultraviolet light, ozone, agitation and aeration are various ageing methods. Once the wine has been aged, it is ready to be put into bottles, where it may continue to slowly age for many years. Most medium- to large-sized wineries now use automated bottling machines, and most moderately priced and expensive wine bottles have corks made of a special oak. The corks are covered with a peel-

off aluminum foil or plastic seal. Cheaper wines have an aluminum screw-off cap or plastic stopper. The corks and screw caps keep the air from spoiling the wine. Wine is usually shipped in wooden crates. However, cheaper wines may be packaged in cardboard.

SELF-ASSIGNMENT EXERCISE

- i. Define oenology
- ii. Describe in details the industrial process of manufacturing wine.

4.0 CONCLUSION

The wine-making process can be done in four steps which are harvesting and crushing grapes, fermenting must, ageing the wine and packaging

5.0 SUMMARY

In this unit, you have learnt in details the manufacturing process of wine. Wines are prepared by the fermentation of fruit juices, most important of which is grape juice. The type of grapes used influences the flavour, colour, alcohol content and acidity of wine. Red and white wine production is basically the same except for one primary difference: the presence of the grape skins during fermentation. The wine-making process involves Harvesting and crushing grapes, Fermenting must, Ageing the wine and Packaging. After crushing and fermentation, it is stored, filtered, and properly aged. Good sweet wine can be obtained by a quick ageing method in about four months. Pasteurization, refrigeration, sunlight, ultraviolet light, ozone, agitation and aeration are various ageing methods. Both red and white wines appear cloudy after fermentation, and the wine maker must wait for the yeast and other solids to settle to the bottom of the fermentation tank, forming sediment called the *lees*. Crushing and fermentation is followed by storage, filtration and proper aging. Pasteurization, refrigeration, sunlight, ultraviolet light, ozone, agitation and aeration are various ageing methods.

6.0 TUTOR- MARKED ASSIGNMENT

State the differences in the making of beer and wine

7.0 REFERENCES/FURTHER READING

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UNIT 4 PHARMACEUTICALS

3.1.1 Production of Penicillin

https://www.youtube.com/watch?v=oWYgM5_YVc0

3.1.2 Production of Tetracycline

https://www.youtube.com/watch?v=oWYgM5_YVc0

3.3.1 Production of Acetylsalicylic acid (Aspirin)

<https://www.youtube.com/watch?v=6lFQaxiRAmI>

3.3.2 Production of Ibuprofen

<https://www.youtube.com/watch?v=hyAVwgKVhDo>

3.3.3 Production of Acetaminophen

<https://www.youtube.com/watch?v=xY33L8SqMo4>

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 - 3.3.2 Production of Ibuprofen
 - 3.3.3 Production of Acetaminophen
- 4.0 Conclusion
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1.0 INTRODUCTION

Pharmaceuticals are compounds manufactured for use as medicinal drugs. They are produced either synthetically or biosynthetically. The major manufactured groups include antibiotics such as penicillin, streptomycin, tetracycline, chloramphenicol, and anti-fungal. Antibiotics are chemical substances that can inhibit the growth of, and

even destroy harmful microorganisms. In this unit, you will learn about the production of penicillin, acetyl salicylic acid and tetracycline.

2.0 OBJECTIVES

By the end of this unit, you should be able to:

- define and give examples of antibiotics.
- describe the industrial production of penicillin.
- describe the industrial production of acetylsalicylic acid (aspirin)
- describe the industrial production of tetracycline
- draw the chemical structures of some antibiotics and analgesics.

3.0 MAIN CONTENT

3.1 Antibiotics

Antibiotics are specific chemical substances derived from or produced by living organisms that are capable of inhibiting the life processes of other organisms. The first antibiotic was discovered in 1896 by Ernest Duchene and rediscovered by Alexander Flemming in 1928 from *Penicillium notatum*. There are over 10,000 different antibiotics known while about 200 are in commercial use. Antibiotics are known to be the most prescribed drugs. Antibiotics are produced on an industrial scale using a variety of fungi and bacteria. Examples include penicillin, ampicillin, amoxicillin, streptomycin, chloramphenicol, cephalosporin, tetracycline, vancomycin etc.

3.1.1 Production of Penicillin

Penicillin was the first naturally occurring antibiotic discovered. It can be obtained in a number of forms from *Penicillium* moulds. It is not a single compound but a group of closely related compounds, all having the same basic ring-like structure (a β -lactam) derived from two amino acids (valine and cysteine) via a tripeptide intermediate. The third amino acid of this tripeptide is replaced by an acyl group (R). Penicillin can be found in two distinctive types: Natural and Semi-synthetic. Penicillin-G is the most potent of all penicillin derivatives. Antibiotics are produced on an industrial scale using a variety of fungi and bacteria. Penicillin is produced by the fungus, *Penicillium chrysogenum*, which requires lactose, other sugars, and a source of nitrogen in the medium to grow well. Penicillin like all antibiotics is a secondary metabolite; hence it is only produced in the stationary phase. It requires a batch fermenter, and a fed batch process is normally used to prolong the stationary period and so increase production. The industrial production of penicillin can be divided into three phases which are:

- Inoculum build up phase
- Growth phase
- Penicillin production phase

Media Formulation:

- Lactose: 1%
- Calcium Carbonate: 1%
- Corn steep liquor: 8.5 %
- Glucose: 1% Phenyl acetic acid: 0.5 g
- Sodium hydrogen phosphate: 0.4 %
- Antifoaming agent: Vegetable oil

At the start of the fermentation process, a number of spores will be introduced into a small conical flask (250-500 ml) where it will be incubated for several days. The most desired parameter at this stage is explosive growth; hence the medium in the flask will contain high amounts of easily utilizable carbon and nitrogen sources such as starch and corn steep liquor. At this stage, the spores begin to revive and form vegetative cells. The conical flask is placed on a shaker to improve oxygen diffusion in the flask. Once the overall conditions for growth have been established and there is a viable vegetative culture active inside the flask, it will be transferred to a 1 or 2 litre bench top reactor. This reactor will be fitted to allow better observation of the culture than when it was in the flask. The cells at this point are expected to be showing filamentous morphology. After a while, the medium being added to the reactor changes. Carbon and nitrogen will now be added sparingly alongside precursor molecules for penicillin fed-batch style. It is important to note that the presence of penicillin in the reactor is itself inhibitory to penicillin production. Hence, it is important to have an efficient method for the removal of this product and to maintain constant volume in the reactor. The penicillin then undergoes downstream processing. The penicillin product needs to be very pure, since it is being used as a therapeutic medical drug, so it is dissolved and then precipitated as a potassium salt to separate it from other substances in the medium. It can then be refined and packaged for marketing and distribution.

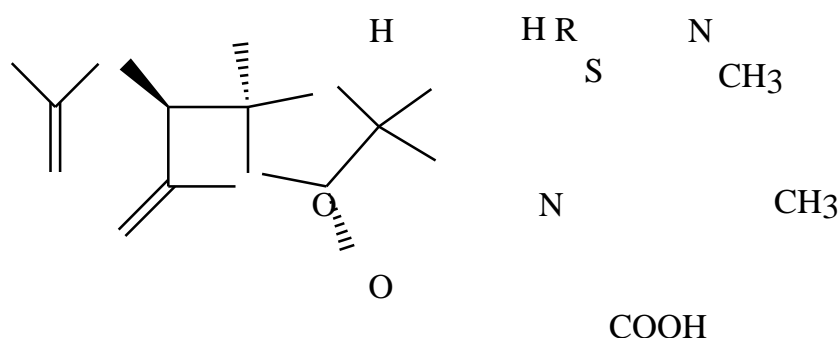


Fig 1: Penicillin structure, "R" is the variable group

3.1.2 Production of Tetracycline

Tetracyclines are antibiotics which are produced by the pharmaceutical industry. Pfizer were the original producers of the first tetracyclines and are the main choice when the proprietary band is prescribed. The production of antibiotics is said to be a batch process, as contamination would be more likely within a continuous process. Although a continuous process is quicker, the wastage caused by contamination means it isn't a cost effective process. Fermentation is used to allow the selected microorganisms to multiply and produce the antibiotic on a large scale. The selected organism which produces the antibiotic is isolated and a starter culture is made to increase the number of available organisms. Next, the medium is transferred to fermentation tanks where the microorganisms are allowed to grow and multiply, so large amounts of the antibiotic are produced. After a number of days, a maximum level of antibiotic will have been produced by the microorganisms and separation of the products can begin. Various different purification methods can be used e.g. organic chemicals, leaving a purified powder. This whole process takes a few days meaning huge quantities can be manufactured each year worth millions of pounds to the producers.

Different formulations are then produced such as tablets, capsules, intravenous drips. The type of formulation will affect how much the drug will cost the customer. For example, tablets are the cheapest as they are the easiest to produce and they are combined with cheap materials and chemicals in formulation. Conversely, an intravenous preparation will be more expensive as a solvent is used to dissolve the drug.

In the production process of tetracycline, the major cost of the materials is in the production of the fermentation culture. It contains essential ingredients that the microorganisms need for growth and reproduction. Most importantly, there will be a carbon source

(molasses/ sugars). Nitrogen is also essential mostly in metabolic pathways which take place in the organism. Other elements such as phosphorus, iron, and copper are also necessary. These are added as salts. Also, to prevent foaming during fermentation, anti-foaming agents such as octadecanol are used.

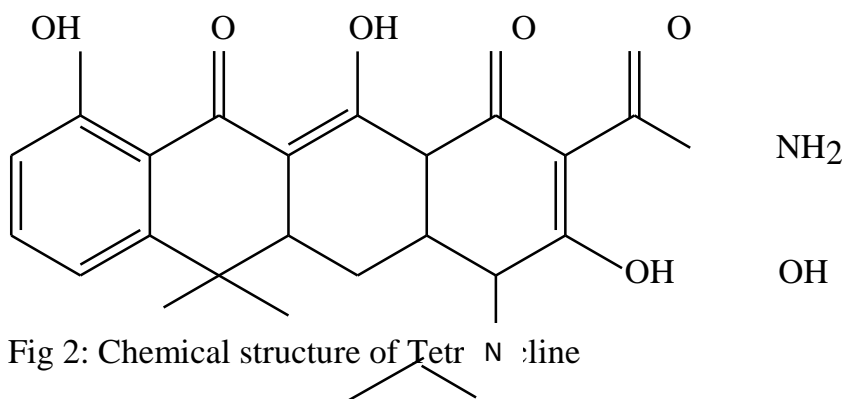


Fig 2: Chemical structure of Tetracycline

Modern Production Method of Penicillin

Significant improvements in modern production methods have increased production and decreased the cost of penicillium. Today, commercial producing strains of penicillium chrysogenum are grown using submerged culture in constantly agitating and aerated 50,000-gallon stainless steel tanks. These industrial strains can now produce 40 – 50 grams of penicillin per litre of culture with 90% recovery yield. This is an overwhelming improvement from the earliest period farmers' market strain that only produced rates, modern penicillin strains display a host of genetic and cellular modifications that result in increased production, including amplification of penicillin biosynthesis gene cluster, an increased number of peroxisome and elevated levels of transporter proteins that secrete newly produced penicillin out of the peroxisomes and the cell.

3.2 Antibacterials

Anti-bacterials act against bacterial infection either by killing the bacterium or by arresting its growth. They do this by targeting bacterial DNA and its associated processes, attacking bacterial metabolic processes including protein synthesis, or interfering with bacterial cell wall synthesis and function. Notable examples of anti-bacterial are Sulfisoxazole and Trimethoprim.

3.2.1 Sulfisoxazole

Sulfisoxazole is a short-acting sulfonamide antibacterial with activity against a wide range of gram-negative and gram-positive organisms. It

is a synthetic analog of para-aminobenzoic acid (PABA) with antibacterial property. It competes with PABA for the bacterial enzyme dihydropteroate synthase, thereby preventing the incorporation of PABA into dihydrofolic acid, the immediate precursor of folic acid. This leads to an inhibition of bacterial folic acid synthesis and de novo synthesis of purines and pyrimidines, ultimately resulting in cell growth arrest and cell death. The structure of Sulfisoxazole is given below.

3.2.2 Trimethoprim

Trimethoprim eliminates bacteria that cause urinary tract infections. It is used in combination with other drugs to treat certain types of pneumonia. It also is used to treat traveler's diarrhea. It may also have prophylactic applications, for example in patients receiving biologic agents during inflammation. Trimethoprim can be synthesized by condensing 3, 4, 5-trimethoxybenzaldehyde with ethyl cyanoacetate which gives an ylidene derivative in a Knoevenagel reaction. The double bond in the product formed is reduced by hydrogen over a palladium on carbon catalyst, giving 3, 4, 5-trimethoxybenzylcyanoacetic ester. Reacting this in a heterocyclization reaction with guanidine gives the desired trimethoprim.

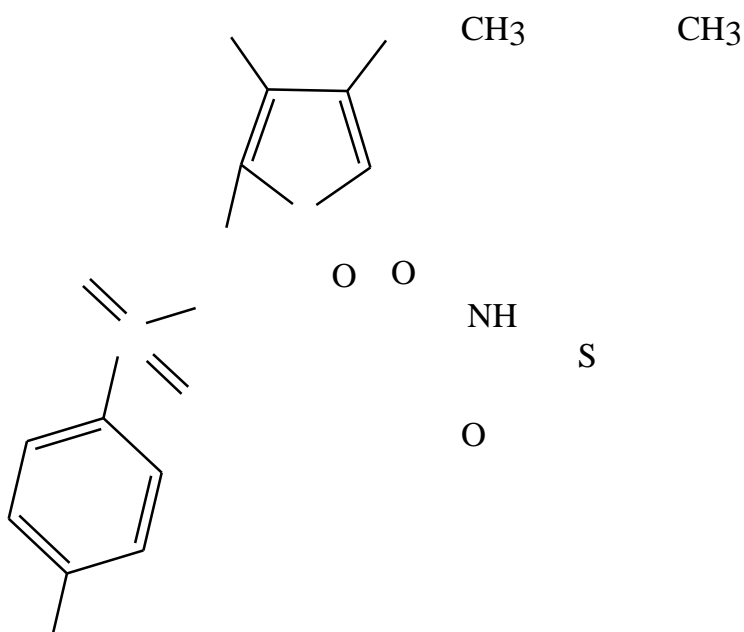


Fig 3: Sulfisoxazole

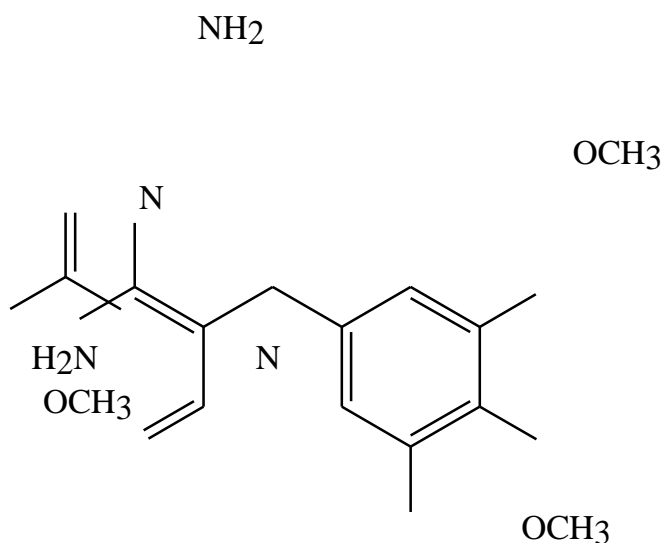


Fig 4: Trimethoprim

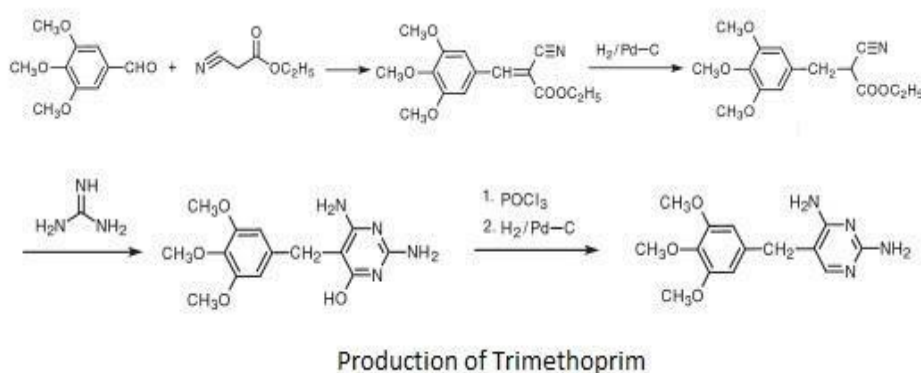


Fig 5: Production scheme of Trimethoprim

3.3 Analgesics

Analgesics are groups of drugs used to achieve relief from pain. Aspirin is a common type of analgesic. It is also an antipyretic, that is, it lowers abnormally high body temperatures. Salicylic acid has been known for its analgesic properties since the early 1800s.

3.3.1 Production of Acetylsalicylic acid (Aspirin)

Acetylsalicylic acid or aspirin is a popular pain-relieving drug (analgesic) developed in the late 19th century as a household remedy for aches and pains. Aspirin tablets are manufactured in different shapes. Their weight, size, thickness, and hardness may vary depending

on the amount of the dosage. The upper and lower surfaces of the tablets may be flat, round, concave, or convex to various degrees. The tablets may also have a line scored down the middle of the outer surface, so the tablets can be broken in half, if desired. The tablets may be engraved with a symbol or letters to identify the manufacturer.

The synthesis of aspirin is classified as an esterification reaction, where the alcohol group from the salicylic acid reacts with an acid derivative (acetic anhydride), yielding methyl acetyl ester and acetic acid as a by-product. Small amounts of sulphuric acid are often used as a catalyst. The main reactor for the process is a glass-lined 1500-gallon tank fitted with a water-cooled reflux condenser, thermometers with automatic temperature registers, and an efficient agitator. The reactor is charged with mother liquor. The mother liquor is prepared by dissolving 1532 kg of acetic anhydride in 1200 kg of toluene. The toluene is a solvent which does not participate in the reaction and so can be recovered later and reused. 1382 kg of Salicylic acid is added to the mother liquor in the reactor. The reaction mixture is heated to between 88 and 92 °C. It is kept at this temperature for twenty hours. Next, the reaction mixture is transferred to aluminum cooling tanks and is allowed to cool for 3 to 4 days. By the end of cooling, the mixture has reached room temperature, approximately 15 to 25 °C.

At this point, the acetylsalicylic acid has precipitated as large regular crystals. The mother liquor is now removed through filtration or centrifuging to separate out as much liquid as possible. The filtrate will be a solution of 180 to 270 kg of unprecipitated acetylsalicylic acid, 510 kg of acetic anhydride, 600 kg of acetic acid and 1200 kilograms of toluene. The acetic acid is obtained as a by-product of the acetylation step of the process. Next, ketene gas is passed through the recycled filtrate at a temperature of 15 to 25 °C. The gas is introduced into a well agitated reactor using a diffusion plate or sparger. This continues until there is a weight increase of 420.5 kg of ketene is observed. At this point, the mother liquor contains 180 to 270 kg of unprecipitated acetylsalicylic acid and 1532 kg of acetic anhydride in 1200 kg of toluene. The mother liquor is recycled and 1382 kg of salicylic acid is added to continue the reaction cycle. The acetylsalicylic acid which was extracted after the initial reaction is washed with distilled water until all the acetic acid is removed. It is then pressed or centrifuged as dry as possible and then dried more by a current of warm air at 60 to 70 °C. The yield of pure acetylsalicylic acid is between 1780 to 1795 kg per batch for this reaction process. Documentation on each batch is kept throughout the manufacturing process, and finished tablets undergo several tests before they are bottled and packaged for distribution.

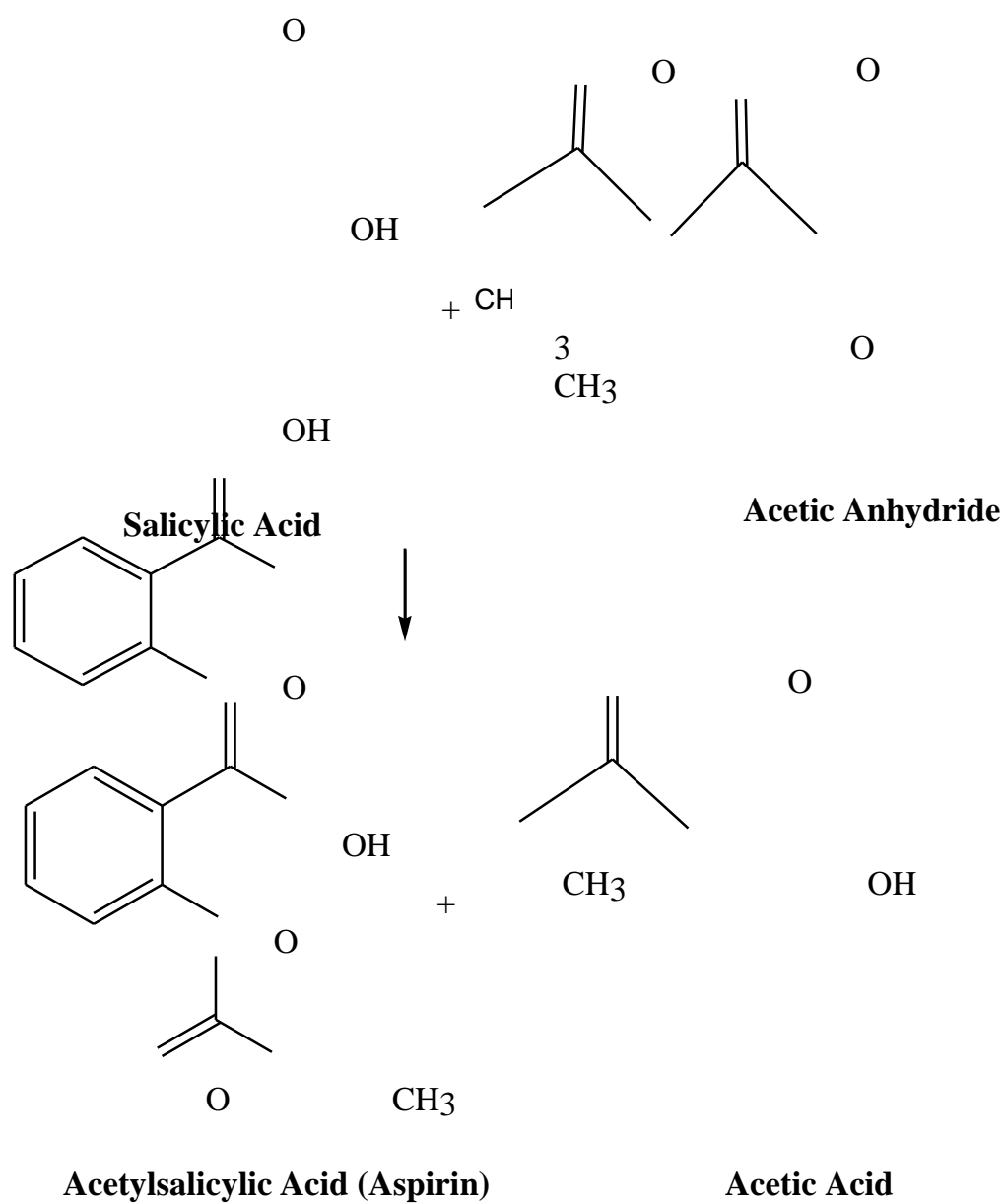


Fig 6: **Production of Acetylsalicylic acid (Aspirin)**

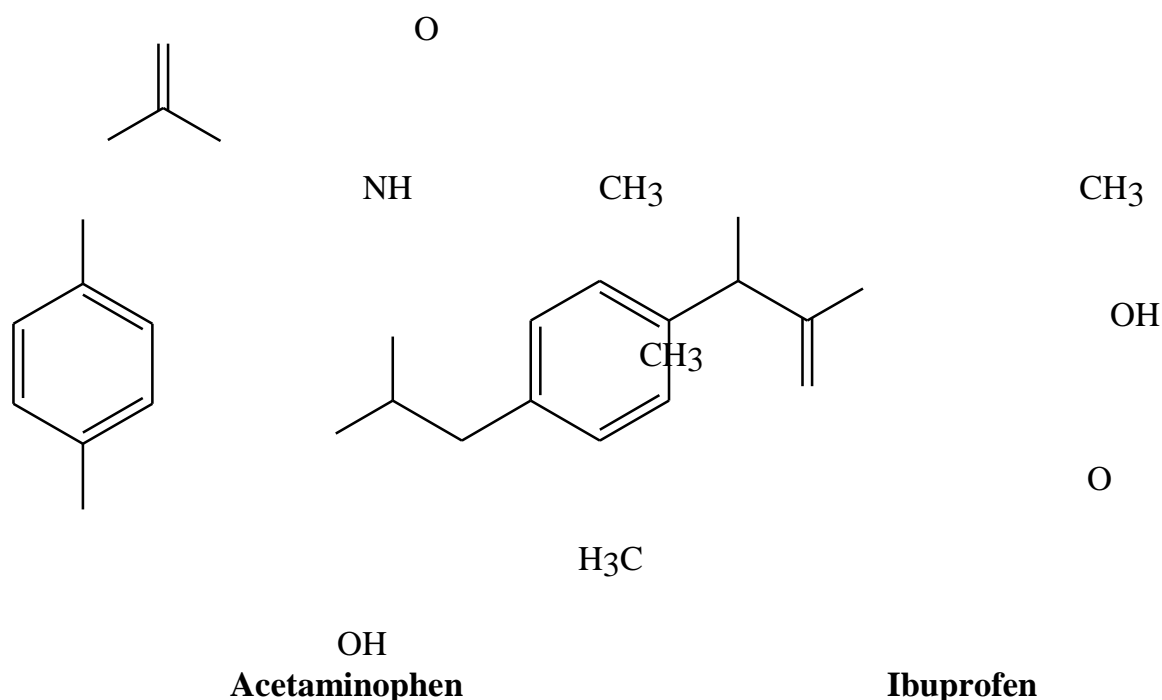


Fig 7: Acetaminophen and Ibuprofen

3.3.2 Production of Ibuprofen

Ibuprofen also has good analgesic and anti-inflammatory action. It is a very popular alternative to aspirin and acetaminophen. Its trade names are Motrin and Advil. It can be synthesized from isobutyl benzene by a Friedel-Crafts acylation with acetyl chloride, followed by formation of cyanohydrins. Treatment with H₂/Pd reduces the benzylic hydroxyl to hydrogen and hydrolysis of the nitrile gives the carboxylic acid.

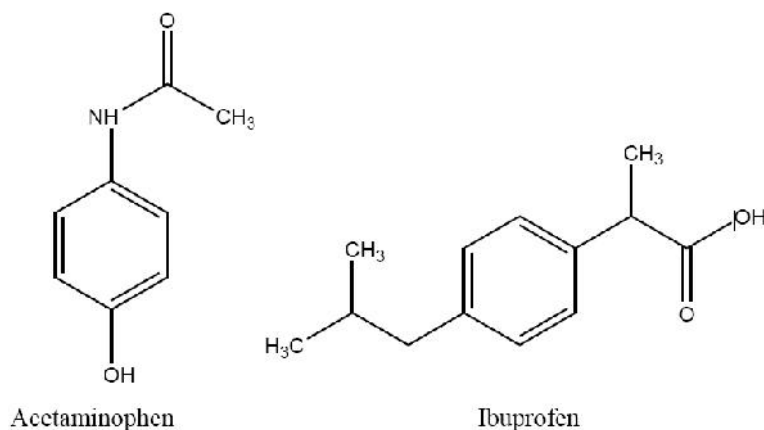
3.3.3 Production of Acetaminophen

A common trademark for acetaminophen is Tylenol. Its common abbreviation is APAP, since its full name is N-acetyl-*p*-aminophenol. Acetaminophen is easily synthesized from phenol by nitration, reduction of the nitro group to an amine, and acetylation.

SELF-ASSIGNMENT EXERCISE

- What do you understand by antibiotic?
- What are the carbon and nitrogen sources in penicillin production process?

- iii. Which antifoaming agent is used in the production of the following antibiotics?
 - (a) Penicillin
 - (b) Tetracycline
- iv. Describe the production process of aspirin.
- v. Draw the chemical structures of the following:
 - (a) Acetaminophen
 - (b) Ibuprofen

No 5**4.0 CONCLUSION**

Antibiotics are produced on an industrial scale using a variety of fungi and bacteria. Antibiotics like penicillin and tetracycline are produced by fermentation method while the production of acetylsalicylic acid is an esterification process.

5.0 SUMMARY

In this unit, you have learnt that antibiotics are the most prescribed drugs. You can now give several examples of antibiotics apart from the common antibiotics you were familiar with. In addition, you have learnt the production processes of penicillin, acetyl salicylic acid and tetracycline. Antibiotics are capable of inhibiting the life processes of other organisms. Examples include penicillin, ampicillin, amoxicillin, streptomycin, chloramphenicol, cephalosporin, tetracycline, vancomycin etc. But Penicillin was the first naturally occurring antibiotic discovered. Tetracyclines are antibiotics which are produced by the pharmaceutical industry. Antibacterials act against bacterial infection either by killing the bacterium or by arresting its growth. Sulfisoxazole is a short-acting sulfonamide antibacterial with activity against a wide range of gram-negative and gram-positive organisms.

Trimethoprim eliminates bacteria that cause urinary tract infections. Analgesics are groups of drugs used to achieve relief from pain. Aspirin is a common type of analgesic. It is also an antipyretic

6.0 TUTOR-MARKED ASSIGNMENT

Draw the chemical structure of the following:

- (a) Aspirin
- (b) Trimethoprim
- (c) Sulfisoxazole
- (d) Tetracycline

7.0 REFERENCES/FURTHER READING

Hare, T and White, L (2011). Penicillin production. Retrieved from <http://microbiologyprocesses.blogspot.com/2011/12/penicillin-production.html>

<http://nobelprize.org/medicine/educational/penicillin/readmore.html>

<http://www.ukessays.co.uk/essays/sciences/tetracyclines-antibiotics>

Production of tetracycline by *Streptomyces aureofaciens* in synthetic media (Downloaded from <http://aem.asm.org/> on February 03, 2020).

MODULE 2

UNIT 1 POLYMERS

3.2.1 Classification of Polymers Based on Nature of Monomer

<https://www.youtube.com/watch?v=q7wH5-BKwQM>

3.2.2 Classification of Polymers Based on Mode of Polymerization

<https://www.youtube.com/watch?v=C379sRPi0R4>

Classification of Polymers Based on Molecular Forces

<https://www.youtube.com/watch?v=czA0FQlfeJc>

UNIT 1 POLYMERS

CONTENTS

- 1.0 Introduction
- 2.0 Objectives
- 3.0 Main Content
 - 3.1 Basics of Polymers
 - 3.2 Classification of Polymers
 - 3.2.1 Based on Nature of Monomers
 - 3.2.1.1 Homopolymers
 - 3.2.1.3 Copolymers
 - 3.2.2 Based on Mode of Polymerization
 - 3.2.2.1 Addition polymers
 - 3.2.2.2 Condensation polymers
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 - 3.2.3.1 Thermoplastics
 - 3.2.3.2 Thermosets
 - 3.3 Applications of polymers
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- 5.0 Summary
- 6.0 Tutor-Marked Assignment
- 7.0 References/Further Reading

1.0 INTRODUCTION

In this unit, you will be introduced to polymers, their properties, and some of the many ways polymers are found in the modern world.

Polymers are long chain giant organic molecules assembled from many smaller molecules called monomers. Polymers consist of many repeating monomer units in long chains. A polymer is analogous to a necklace made from many small beads (monomers).

2.0 OBJECTIVES

By the end of this unit, you should be able to:

- define polymers.
- list and explain the classes of polymers.
- explain the applications of polymers

3.0 MAIN CONTENT

3.1 Basics of Polymers

Polymers are high molecular weight compounds built up by the repetition of small chemical units known as monomers. They are either natural or synthetic. The natural polymers include rubber, cellulose, wool, starch and proteins while the synthetic polymers include nylon, polyethylene, polyvinyl chloride and polyester. The term *polymer* comes from two Greek words: *poly*, meaning “many” and *mer*, meaning “parts.” A polymer is therefore a high molecular weight compound made up of hundreds or thousands of many identical small basic units (monomers) of carbon, hydrogen, oxygen or silicon atoms. The monomers are linked together covalently in a chemical process known as polymerization.

Polymers may be naturally found in plants and animals (natural polymers) or may be man-made (synthetic polymers)

Types of Polymers:

- a) Natural polymers: They occur naturally and are found in plants and animals, for example proteins, starch, cellulose, and rubber. To add up, we also have biodegradable polymers which are called biopolymers.

- b) Semi synthetic polymers: They are derived from naturally occurring polymers and undergo further chemical modification, example cellulose nitrate, cellulose acetate.
- c) Synthetic polymers. These are man-made polymers. Plastic is the most common and widely used synthetic polymer. It is used in industries and various dairy products, example nylon tile, polyethers, etc.

On the basis of the type of the backbone chain polymers can be divided into:

- a) organic polymers: Carbon backbone
- b) Inorganic polymers: Backbone constituted by elements other than carbon

There are also high temperature polymers: These polymers are stable at high temperature. Due to their high molecular weight, they are not destroyed even at very high temperatures. They are extensively used in the healthcare industries for making sterilization equipment and in manufacturing of heat and shock resistance objects.

3.2 Classification of Polymers

3.2.1 Based on Nature of Monomer

Polymers are classified on the basis of nature of monomers linked together into homopolymers and copolymers.

3.2.1.1 Homopolymers

Linear polymers

The structure of polymers containing long and straight chains fall into this category, e.g Polyvinyl Chloride (PVC), which is largely used for making pipes and electric cables.

They consist of chains with identical bonding linkages to each monomer unit. This implies that the polymer is made from all identical monomer molecules.

Homopolymers may be represented as - [A-A-A-A-A-A]-

3.2.1.2 Copolymers

They consist of chains with two or more linkages usually implying two or more different types of monomer units. The synthetic rubber used to make shoe soles, for example, is a copolymer made of the

monomers butadiene and styrene. Copolymers may be represented as-[A-B-A-B-A-B]-

- i Branched chain polymers
When linear chains of a polymer form branches then such polymers are categorized as branched chain polymers, eg low-density polythene.
- ii Cross- linked polymers
They are composed of bifunctional and trifunctional monomers. They have a strange covalent bond in comparison to other linear polymers. Bakelite and melamine are examples in this category.

3.2.2 Based on Mode of Polymerization

Polymers are further classified by the reaction mode of polymerization into addition polymers and condensation polymers.

3.2.2.1 Addition Polymers

When monomers just add on to form the polymer, the process is called addition polymerization. The polymer is the only product e.g. Ethylene monomers add on to form polyethylene. The monomer molecules bond to each other without the loss of any other atoms. The biggest groups of polymers in this class are the alkene monomers. This class of polymers accounts for a large proportion of the synthetic polymer industry and includes the large-tonnage materials such as polyethene, polystyrene, polyvinylchloride (PVC) and acrylics. The mechanism of the reaction for all these is the ring opening of the double bond in an alkene to give an all-carbon backbone of single bonds. These type of polymers are also referred to as chain polymers.

3.2.2.2 Condensation Polymers

Here, two different monomer molecules condense with the loss of a small molecule, usually water to form a polymer. The condensation takes place between two reactive functional groups, like the carboxyl group (of an acid) and the hydroxyl group (of an alcohol). Polyesters and polyamides (nylon) are in this class of polymers. This type of polymers is also referred to as step growth polymers. An example is given below:

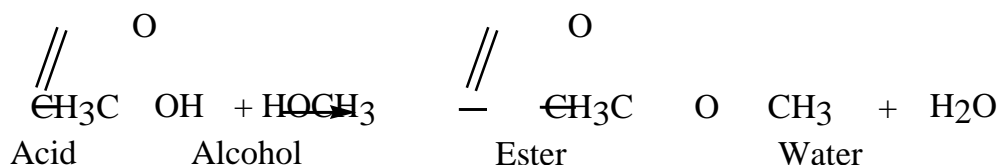


Fig 8: Ester formation

3.2.3 Based on Physical property related to heating

Classification of polymers can also be based upon the physical property related to heating. This classifies them into thermoplastics and thermosets.

3.2.3.1 Thermoplastics

These are plastics that soften when heated and become firm again when cooled. They are more popular because the heating and cooling may be repeated. Thermoplasts can be shaped and melted over and over again. Examples of thermoplastics include acetal, acrylic, cellulose acetate, polyethylene, polystyrene, vinyl, and nylon.

3.2.3.2 Thermosets

These are plastics that soften when heated and can be molded, but harden permanently. Thermosets can be melted and shaped only once. If heated a second time, they tend to crack or disintegrate. Examples of thermosets include amino, epoxy, and phenolic and unsaturated polyesters.

Classification Based on Molecular Forces

- i) Elastomers: These are rubber like solids, weak interaction forces are present, for example rubber
- ii) Fibers: Strong, tough, high tensile strength and strong forces of interaction are present, eg nylon-66
- iii) Thermoplastics: These are having intermediate forces of attraction, eg PVC
- iv) Thermosetting polymers: These polymers greatly improve the materials mechanical properties. It provides enhanced chemical and heat resistance, phenolics, epoxies and silicone.

3.3 Applications of Polymers

Polymers have applications in Agriculture, Medicine, Consumer Science, Industry and Sports.

3.3.1 Agriculture

Polymeric materials are used in and on soil to improve aeration, provide mulch, and promote plant growth and health. Polymers have revolutionized the agricultural and food industry with new tools for the molecular treatment of diseases, rapid disease detection and enhancing the ability of plants to absorb nutrients. Functionalized polymers were used to increase the efficiency of pesticides and herbicides, allowing lower doses to be used and to protect the environment indirectly through filters or catalysts to reduce pollution and clean-up existing pollutants.

3.3.2 Medicine

Many biomaterials, especially heart valve replacements and blood vessels, are made of polymers like Dacron, Teflon and polyurethane. Examples of newer medical applications of polymeric materials include controlled drug delivery, polymeric drugs, and artificial skin.

3.3.3 Consumer Science

Plastic containers of all shapes and sizes are light weight and economically less expensive than the more traditional containers. Clothing, floor coverings, garbage disposal bags, and packaging are other polymer applications.

3.3.4 Industry

Automobile parts, windshields for fighter planes, pipes, tanks, packing materials, insulation, wood substitutes, adhesives, matrix for composites, and elastomers are all polymer applications used in the industrial market.

3.3.5 Sports

Playground equipment, various balls, golf clubs, swimming pools, and protective helmets are often produced from polymers.

SELF-ASSIGNMENT EXERCISE

- i. Explain the applications of polymers.
- ii. List and explain the classes of polymers.
- iii. Differentiate between addition and condensation polymers.

4.0 CONCLUSION

There are several ways to classify polymers. Also, polymers can be found in the modern world in the fields of Agriculture, Medicine, Consumer Science, Industry and Sports.

5.0 SUMMARY

In this unit, you have learnt the following:

- Polymers are high molecular weight compounds built up by the repetition of small chemical units known as monomers.
- Polymers can be classified on the basis of nature of monomers, mode of polymerization and physical property related to heating.
- Polymers have applications in Agriculture, Medicine, Consumer Science, Industry and Sports.
- Organic and inorganic polymers, natural polymers, semi synthetic polymers, synthetic polymer as types of polymers, Fibers, Thermoplastics

6.0 TUTOR-MARKED ASSIGNMENT

Other than those mentioned, list other applications of polymer

7.0 REFERENCES/FURTHER READING

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UNIT 2 POLYETHYLENE

3.1 Classification of Polyethylene

https://www.youtube.com/watch?v=cir_bVysyX0

3.2 Production Process of Polyethylene

https://www.youtube.com/watch?v=U6d_F1jcKzI

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 - 3.1.1 High Density Polyethylene (HDPE)
 - 3.1.2 Low density polyethylene (LDPE)
 - 3.1.3 Linear low density polyethylene (LLDPE)
 - 3.2 Production Process of Polyethylene
 - 3.2.1 High Pressure Production Process
 - 3.2.2 Low pressure Production Process
- 5.0 Conclusion
- 6.0 Summary
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1.0 INTRODUCTION

The word “polyethylene” means repeating units of ethylene. These invisibly tiny parts of ethylene (monomers) are the building blocks for polyethylene during production. Polyethylene is a thermoplastic polymer, which can be melted to a liquid and remolded as it returns to a solid state. The IUPAC name of polyethylene is poly (methylene). The general formula for polyethylene is $(\text{CH}_2 - \text{CH}_2)_n$. Polyethylene is chemically synthesized from molecules that contain long chains of ethylene monomer.

2.0 OBJECTIVES

By the end of this unit, you should be able to:

- list and explain the major classes of polyethylene.

- list and explain the categories of production process of polyethylene.
- highlight the uses of polyethylene.

3.0 MAIN CONTENT

3.1 Classification of Polyethylene

Polyethylene is classified into several different categories based mostly on its density and branching. The mechanical properties of polyethylene depend significantly on variables such as the extent and type of branching, the crystal structure and the molecular weight. There are three major classes of polyethylene. These are low density polyethylene (LDPE), high density polyethylene (HDPE) and linear low density polyethylene (LLDPE).

Polyethylene is also available in other types such as medium-density polyethylene (MDPE), very-low density polyethylene (VLDP), High-molecular-weight polyethylene (HMWPE), ultra-low-molecular weight polyethylene (ULMWPE), chlorinated polyethylene (CPE)

3.1.1 High density polyethylene (HDPE)

This is chemically the closest in structure to pure polyethylene. It consists primarily of unbranched molecules with very few flaws to mar its linearity. With an extremely low level of defects to hinder organization, a high degree of crystallinity can be achieved, resulting in resins that have a high density (relative to other types of polyethylene). Some resins of this type are copolymerized with a very small concentration of 1-alkenes in order to reduce the crystallinity level slightly. High density polyethylene resins typically have densities falling in the range of approximately $0.94\text{--}0.97\text{ g/cm}^3$. Due to its very low level of branching, high density polyethylene is sometimes referred to as linear polyethylene (LPE).

3.1.2 Low density polyethylene (LDPE)

Low density polyethylene (LDPE) is so named because such polymers contain substantial concentrations of branches that hinder the crystallization process, resulting in relatively low densities. The branches primarily consist of ethyl and butyl groups together with some long chain branches. Due to the nature of the high pressure polymerization process by which low density polyethylene is produced, the ethyl and butyl branches are frequently clustered together, separated by lengthy runs of unbranched backbone. Long chain branches occur at random intervals along the length of the main chain. The long chain

branches can themselves in turn be branched. The numerous branches characteristic of low density polyethylene molecules inhibits their ability to crystallize, reducing resin density relative to high density polyethylene. Low density polyethylene resins typically have densities falling in the range of approximately 0.90–0.94 g/cm³

Applications of High Density Polyethylene (HDPE)

- i. Packaging- High density polyethylene is used in several packaging applications including crates, trays, and bottles for milk and fruits juices, caps for food packaging, jerry cans, drums, industrial bulk containers etc.
- ii. Consumer goods-Low cost and easy processibility make hope a material of choice in several household/ consumer goods like garbage containers, housewares, ice boxes, toys etc
- iii. Fibers and textiles: They have high tensile strength and therefore widely used in ropes in ropes, fishing and sports nets, for agricultural use, industrial and decorative fabrics etc.
- iv. Other application of HOPE include pipes, and fittings, sea outfalls, industrial application, cable protection etc

3.1.3 Linear low density polyethylene (LLDPE)

Linear low density polyethylene (LLDPE) resins consist of molecules with linear polyethylene backbones to which are attached short alkyl groups at random intervals. These materials are produced by the copolymerization of ethylene with 1-alkenes. The branches most commonly encountered are ethyl, butyl, or hexyl groups but can be a variety of other alkyl groups, both linear and branched. A typical average separation of branches along the main chain is 25–100 carbon atoms. Linear low density polyethylene resins may also contain small levels of long chain branching, but there is not the same degree of branching complexity as is found in low density polyethylene. Chemically these resins can be thought of as a compromise between linear polyethylene and low density polyethylene, hence the name. The branches hinder crystallization to some extent, reducing density relative to high density polyethylene. The result is a density range of approximately 0.90–0.94 g/cm³.

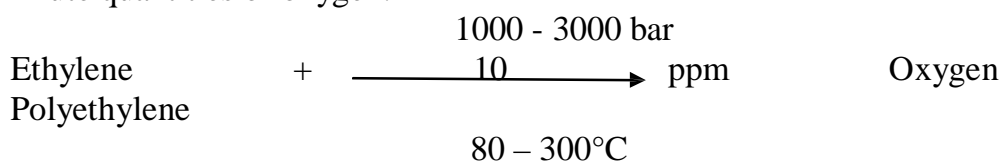
3.2 Production Process of Polyethylene

Polyethylene manufacturing process is categorized into “high pressure” and “low pressure” operations. The high pressure is generally recognized as producing conventional low density polyethylene (LDPE) while the low pressure makes high density polyethylene (HDPE) and linear low density polyethylene (LLDPE).

3.2.1 High Pressure Production Process

The polyethylene products known as low density polyethylene (LDPE) resins are produced exclusively by high pressure free radical polymerization. The chemistry involved in their production is deceptively simple, requiring little more than an appropriate source of free radicals and conditions of high temperature and pressure. The free radicals initiate the polymerization process when the monomers have been forced into close proximity by high pressure. Termination of chain growth occurs when the free radical on a growing chain is transferred to another chain or is quenched by another radical. In practice, numerous competing side reactions occur that result in branching and premature chain termination. The nature of the product is controlled by the initiator concentration, temperature, pressure, availability of vinyl co monomers, and the presence of chain transfer agents.

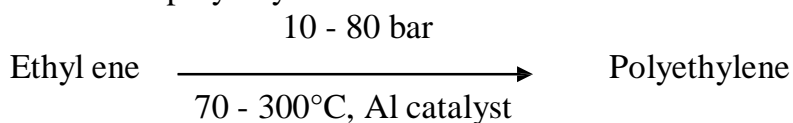
Polyethylene was first produced by the high pressure process in the 1930's. It was discovered that ethylene gas could be converted into a white solid by heating it at very high pressures in the presence of minute quantities of oxygen:



The polymerization reaction which occurs is a random one, producing a wide distribution of molecule sizes. By controlling the reaction conditions, it is possible to select the average molecule size (or molecule weight) and the distribution of sizes around this average (molecular weight distribution). The chains are highly branched (at intervals of 20 – 50 carbons). This new plastic was named “polythene” and was produced in a density range of about 0.915 to 0.930 g cm³. It is known today as LDPE and has its single biggest usage in blown film.

3.2.2 Low Pressure Production Process

The polymerization of ethylene at much lower pressures also results in the manufacture of polyethylene.



HDPE is produced by three types of process which are slurry process, solution process and gas phase process. All operate at

relatively low pressures (10-80 atm) in the presence of a Ziegler-Natta or inorganic catalyst. In all the three processes, hydrogen is mixed with ethene to control the chain length of the polymer.

The product from this process was found to be much stiffer than previous products and had a density range of about 0.940 to 0.970 g cm³. The increased stiffness and density were found to be due to a much lower level of chain branching. The new HDPE was found to be composed of very straight chains of ethylene with a much narrower distribution of molecular weights (or chain lengths) and a potentially very high average chain length.

The low pressure process was also applied to the production of LLDPE. LLDPE is made by copolymerizing of ethylene with a small amount of another monomer, typically butene, hexene or octene. The most common method used in industry is to polymerize ethylene by means of a fluidized reactor bed. A fluidized reactor bed consists of metallic catalyst particles that are 'fluidized' by the flow of ethylene gas. This means that the catalyst particles are suspended in the ethylene fluid as ethylene gas is pumped from the bottom of the reactor bed to the top.

Before ethylene is sent to the fluidized bed, it must first be compressed and heated. Pressures in the range of 100-300 pounds per square inch (psi) and a temperature of 100°C are necessary for the reaction to proceed at a reasonable rate. The catalyst is also pumped with the ethylene stream into the reactor. This is because polyethylene molecules remain stuck to the catalyst particle from which they were produced thus incorporating the catalyst within the polyethylene product. Hence the need to replenish the "consumed" catalyst.

The conversion of ethylene is low for a single pass through the reactor and it is necessary to recycle the unreacted ethylene. Unreacted ethylene gas is removed off the top of the reactor. After purification, ethylene gas is then recompressed and recycled back into the reactor. Granular polyethylene is gradually removed from the bottom of the reactor as soon as reasonable conversions have been achieved. Typically, residence time of 3 to 5 hours results in a 97% conversion of ethylene. Polyethylene comes out of reactor as granular powder, which is then melted and flows through a film extruder. Whatever the type of polyethylene produced, the end product is usually available in the form of small pellets, varying in shape (spherical rectangular, cylindrical) depending upon the manufacturer's equipment. During the manufacture of polythene products, it is melted to flow through a film extruder.

LDPE is the preferred packaging material due to its limp feel, transparency, toughness, and the ability to rapidly take up the shape of

the contents of the bag. The garbage bag is just one of many widely practical uses of plastic bags. Polyethylene film, produced by blown film extrusion, is commonly used for packaging of foodstuffs and other products. The thickness of the film produced tends to be from 20 - 200 μm .

3.3 Uses of Polyethylene

- The LDPE or LLDPE form is preferred for film packaging and for electrical insulation.
- HDPE is blow-moulded to make containers for household chemicals such as washing-up liquids and drums for industrial packaging.
- HDPE is also extruded as piping.

SELF –ASSESSMENT EXERCISES

- i. Explain the following:
 - (a) Low pressure production of polyethylene
 - (b) High pressure production of polyethylene
- ii. List and explain the three major classes of polyethylene
- iii. Mention five uses of polyethylene

4.0 CONCLUSION

The classes of polyethylene, the two different production operations viz high pressure and low pressure as well as the uses have been discussed. HDPE is produced by three types of process which are slurry process, solution process and gas phase process. All operate at relatively low pressures (10-80 atm) in the presence of a Ziegler-Natta or inorganic catalyst. The low pressure process was also applied to the production of LLDPE. LLDPE is made by copolymerizing of ethylene with a small amount of another monomer, typically butene, hexene or octene. The conversion of ethylene is low for a single pass through the reactor and it is necessary to recycle the unreacted ethylene. Unreacted ethylene gas is removed off the top of the reactor. After purification, ethylene gas is then recompressed and recycled back into the reactor.

5.0 SUMMARY

In this unit, you have learnt the following:

- The three major classes of polyethylene are low density polyethylene (LDPE), high density polyethylene (HDPE) and linear low density polyethylene (LLDPE).

- Polyethylene can be produced via the high pressure or low pressure operations.
- The high pressure operation produces low density polyethylene (LDPE) while the low pressure produces high density polyethylene (HDPE) and linear low density polyethylene (LLDPE).
- Polyethylene is used for electrical insulation, for making household chemicals, for making drums for industrial packaging etc.

6.0 TUTOR-MARKED ASSIGNMENT

List all the possible home and domestic appliances made of Polyethylene

7.0 REFERENCES/FURTHER READING

Nicholson, J. W. (2006). The Chemistry of Polymers. Third Edition. London, UK: Royal Society of Chemistry.

<http://www.essentialchemicalindustry.org/polymers.html> [Assessed July 05, 2020]

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UNIT 3 STYRENE BUTADIENE RUBBER

3.2 Types of Styrene butadiene rubber (SBR)

<https://www.youtube.com/watch?v=IjAbgjVuveg>

3.3 Emulsion SBR Polymerization Process.

<https://www.youtube.com/watch?v=fa-NyQQ1AY0>

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- 1.0 Introduction
- 2.0 Objectives
- 3.0 Main Content
 - 3.1 Structural Formula of Styrene Butadiene Rubber
 - 3.2 Types of Styrene butadiene rubber (SBR)
 - 3.2.1 Emulsion SBR
 - 3.2.2 Solution SBR
 - 3.3 Emulsion SBR Polymerization Process
 - 3.4 Solution SBR Polymerization Process
 - 3.5 Applications of Styrene Butadiene Rubber
- 4.0 Conclusion
- 5.0 Summary
- 6.0 Tutor-Marked Assignment
- 7.0 References/Further Reading

1.0 INTRODUCTION

Styrene butadiene rubber (SBR) describes families of synthetic rubbers derived from styrene and butadiene. These materials have good abrasion resistance and good aging stability when protected by additives. In 1929, E. Tschunkur and A. Bock discovered that mixtures of butadiene and styrene in a 75:25 ratios can be copolymerized in emulsion. The styrene/butadiene ratio influences the properties of the polymer; with high styrene content, the rubbers are harder and less rubbery. In 1930, the first emulsion polymerized SBR known as Buna S was prepared by I. G. Farben, a leading chemical industry in Germany. Buna S derives Bu from butadiene and Na from sodium and S from Styrene.

2.0 OBJECTIVES

By the end of this unit, you should be able to:

- Give the structural formula of Styrene Butadiene Rubber.
- Explain the types of Styrene Butadiene Rubber.
- Describe the production processes of emulsion-SBR and solution-SBR.

3.0 MAIN CONTENT

SBR is very economical and possesses no unique chemical resistance properties. It can be compounded to provide very fine abrasion, wear and tensile qualities. It can be substituted for natural rubber in many applications with significant cost savings. Its resilience is about the same as natural rubber. It is a good choice when deciding to choose a material that has great mechanical properties and flexibility.

3.1 Structural Formula of Styrene Butadiene Rubber

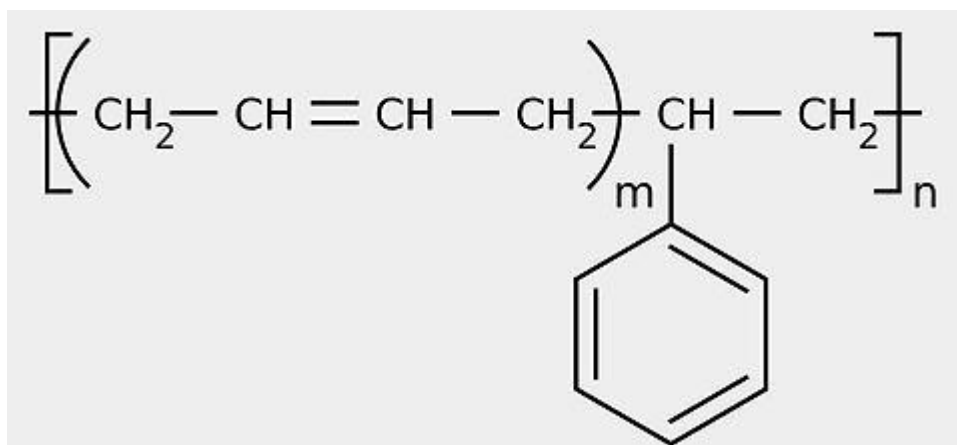


Fig 9: Styrene Butadiene Rubber

3.2 Types of Styrene butadiene rubber (SBR)

There are two major types of SBR, Emulsion SBR (E-SBR) and Solution SBR (S-SBR), based on the different manufacturing process.

3.2.1 Emulsion SBR

Emulsion-SBR (E-SBR) produced by emulsion polymerization is initiated by free radicals. The emulsion polymerization process has several advantages. It is normally used under mild reaction conditions that are tolerant to water and requires only the absence of oxygen. The process is relatively robust to impurities and amenable to using a range of functionalized and non-functionalized monomers. Additional benefits include the fact that emulsion polymerization gives high solids contents with low reaction viscosity and is a cost-effective process. The physical state of the emulsion (colloidal) system makes it easy to

control the process. Thermal and viscosity problems are much less significant than in bulk polymerization.

E-SBRs produced at low polymerization temperatures have less chain branching than those produced at higher temperature. The styrene content of most emulsion SBR varies from 0% to 50%. The percent styrene of most commercially available grades of E- SBR is 23.5%.

3.2.2 Solution SBR

Solution-SBR is produced by an anionic polymerization process. Polymerization is initiated by alkyl lithium compounds. Water is strictly excluded. The process is homogeneous (all components are dissolved), which provides greater control over the process, allowing tailoring of the polymer. The organo-lithium compound adds to one of the monomers, generating a carbanion that then adds to another monomer, and so on. Relative to E-SBR, S-SBR is increasingly favored because it offers improved wet grip and rolling resistance, which translates to greater safety and better fuel economy. SBR is produced by the copolymerization of butadiene with styrene in the approximate proportion of 3:1 by weight.

3.3 Emulsion SBR Polymerization Process.

The raw materials required in the polymerization of E-SBR include the monomers (styrene and butadiene), water, emulsifier, initiator system, modifier, shortstop and a stabilizer system. The original polymerization reactions are charged out in batch reactors in which all the ingredients are loaded to the reactor and the reaction is shortstopped after it has reached the desired conversion. Current commercial productions are run continuously by feeding reactants and polymerizing through a chain of reactors before shortstopping at the desired monomers conversion. The monomers are continuously metered into the reactor chains and emulsified with the emulsifiers and catalyst agents. In cold polymerization, the most widely used initiator system is the redox reaction between chelated iron and organic peroxide using sodium formaldehyde sulfoxide (SFS) as reducing agent (see equations below).

In hot polymerization, potassium peroxydisulfate is used as an initiator.



Mercaptan is added to furnish free radicals and to control the molecular weight distribution by terminating existing growing chains while

initiating a new chain. The thiol group acts as a chain transfer agent to prevent the molecular weight from attaining the excessively high values possible in emulsion systems. The sulfur-hydrogen bond in the thiol group is extremely susceptible to attack by the growing polymer radical and thus loses a hydrogen atom by reacting with polymer radicals (see equations below). The RS formed will continue to initiate the growth of a new chain. The thiol prevents gel formation and improves the processability of the rubber.



During polymerization, parameters such as temperature, flow rate and agitation are controlled to get the right conversion. Polymerization is normally allowed to proceed to about 60% conversion in cold polymerization and 70% in hot polymerization before it is stopped with a shortstop agent that reacts rapidly with the free radicals. Examples of common shortstopping agents are sodium dimethyl dithio carbamate and diethyl hydroxylamine. Once the latex is properly shortstopped, the unreacted monomers are stripped off the latex. Butadiene is stripped by degassing the latex by means of flash distillation and reduction of system pressure. Styrene is removed by steam stripping the latex in a column. The latex is then stabilized with the appropriate antioxidant and transferred to blend tanks. In the case of oil-extended polymers or carbon black master batches, these materials are added as dispersions to the stripped latex. The latex is then transferred to finishing lines to be coagulated with sulfuric acid, sulfuric acid/sodium chloride, glue/sulfuric acid, aluminum sulfate, or amine coagulation aid. The type of coagulation system is selected depending on the end-use of the product. Sulfuric acid/sodium chloride is used for general purpose. Glue/sulfuric acid is used for electrical grade and low water sensitivity SBR. Sulfuric acid is used for coagulations where low-ash-polymer is required. Amine coagulating aids are used to improve coagulation efficiency and reduce production plant pollution. The coagulated crumb is then washed, dewatered, dried, baled and packaged.

3.4 Solution SBR Polymerization Process

Solution polymerized styrene-butadiene rubber is obtained by a termination-free, anionic living polymerization of styrene and butadiene, carried out in both batch or continuous process enabling production of different dry and oil extended polymers. The process is first based on the purification of solvent and monomers through distillation and adsorption operations as well as blanketing with dry

nitrogen of all chemical mix and feed tanks, in order to ensure the lowest level of poisons detrimental to polymerization reaction.

Dry solvent (cyclohexane or cyclopentane), styrene, initiator, butadiene and other reactants are continuously loaded to the polymerization reactor train or charged batch wise in a specified sequence to the batch polymerization reactors, depending on grades to be produced. Reaction temperature control is enabled by the use of boiling reactor while the using of proper randomizing agent ensures a complete randomness of styrene with the desired level of vinyl unit. The polymerization conditions lead to a practically complete depletion of monomers; at the end of polymerization the living chain ends are terminated by addition of substances which modify the polymer structure; so radial or branched or linear rubber can be obtained in order to match the required properties.

After polymerization completion the solution is then pumped to a blend tank operating at slight pressure. Residual traces of unconverted monomers, together with a portion of the solvent, are flash vaporized, condensed and then recycled to the wet solvent tank, while the concentrated polymer solution is blended in the blends tanks. The blended solution with the antioxidant agents is fed to the stripping section where the solvent is removed by steam distillation in the presence of a dispersing agent aimed to control the crumb size in the slurry. The crumb slurry is then pumped to the finishing unit, where the crumb is dewatered on a shaker screen, being the water partly recirculated to the strippers and partly sent to waste water treatment. The vapours obtained from the stripping section are otherwise condensed and the solvent, separated from water by a decanter, is sent to the wet solvent tank. The dewatered crumbs are dried in two mechanical extruders in series, cooled with air, weighed and baled.

3.5 Applications of Styrene Butadiene Rubber

- The elastomer is used widely in pneumatic tires, shoe heels and soles, gaskets and even chewing gum.
- Emulsion SBR is extensively used in coated papers, being one of the most cost-effective resins to bind pigmented coatings.
- It is also used in building applications, as a sealing and binding agent.
- SBR can be used to 'tank' damp rooms or surfaces.
- It is also used by speaker driver manufacturers as the material for low damping rubber surrounds.
- It is used in great quantities in automobile and truck tires.

SELF-ASSESSMENT EXERCISE

- i. Draw the structure of Styrene Butadiene Rubber. (2) Explain the types of Styrene Butadiene Rubber.
- ii. Describe the production processes of emulsion-SBR and solution-SBR.

4.0 CONCLUSION

Styrene-butadiene rubber (SBR) is a general-purpose synthetic rubber, produced from a copolymer of styrene and butadiene. Exceeding all other synthetic rubbers in consumption it is generally used as an abrasion-resistant replacement for natural rubber.

5.0 SUMMARY

In this unit, you have learnt the following:

There are two major types of SBR, Emulsion SBR (E-SBR) and Solution SBR (S-SBR), based on the different manufacturing process. The emulsion polymerization process has several advantages. It is normally used under mild reaction conditions that are tolerant to water and requires only the absence of oxygen.

Emulsion-SBR is produced by emulsion polymerization while solution-SBR is produced by an anionic polymerization process. The process is homogeneous (all components are dissolved), which provides greater control over the process, allowing tailoring of the polymer. Polymerization is initiated by alkyl lithium compounds. Water is strictly excluded.

Dry solvent (cyclohexane or cyclopentane), styrene, initiator, butadiene and other reactants are continuously loaded to the polymerization reactor train or charged batch wise in a specified sequence to the batch polymerization reactors, depending on grades to be produced.

6.0 TUTOR-MARKED ASSIGNMENT

Compare and contrast the production processes of emulsion-SBR and solution-SBR.

7.0 REFERENCES/FURTHER READING

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MODULE 3

UNIT 1 PESTICIDES

3.3 Production of Pesticide

<https://www.youtube.com/watch?v=k2-9utkVq4k>

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 - 3.2.2 Classification based on the pests controlled
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1.0 INTRODUCTION

Pesticides are chemicals that we use to kill undesirable organisms. When we say undesirable organisms, we are referring to organisms (plants, animals, insects etc.) that are harmful. Some of these organisms or pests eat our crops, while others spread diseases. Weeds for instance can be considered a pest for just growing in the wrong location. Now, when we use some type of chemical to control these pests, that chemical would be considered a pesticide.

2.0 OBJECTIVES

By the end of this unit, you should be able to:

- classify pesticides based on their origin and the pests controlled.
- give examples of important pesticides.
- describe the three steps in the production process of pesticides.

3.0 MAIN CONTENT

3.1 Pesticides

Pesticides are products that destroy various agricultural pests, including weeds (herbicides), insects (insecticides), bacteria (microbicides) and fungi (fungicides). They cause economic damage to crop or ornamental plants and are hazardous to the health of domestic animals or humans. All pesticides interfere with normal metabolic processes in the pest organism and often are classified according to the type of organism they are intended to control. Important pesticides include dichloro diphenyl trichloroethane (DDT), 2, 4-D ethion, malathion, formalin and bio pesticides. Pesticides are nowadays basic need for agricultural production and almost every country in the world uses pesticides. An appreciable amount of food is lost due to insect pests, plant pathogens, weeds, rodents, birds and in storage. Pesticide industry has developed substantially and has contributed significantly towards agricultural and public health.

3.2 Classification of Pesticides

Pesticides can be classified based on their origin and the pests they control.

3.2.1 Classification based on their origin

Pesticides are classified based on their origin into chemical pesticides and bio pesticides.

3.2.1.1 Chemical Pesticides

These are further divided into four types:

- Carbamates
- Organophosphate pesticides
- Organochlorine pesticides
- Pyrethroid pesticides

3.2.1.2 Bio pesticides

These are derived naturally from living organisms or their metabolites like bacteria, fungi, plants etc. They are classified into three major groups:

- Microbial pesticides
- Biochemical pesticides
- Plant incorporated protectants

3.2.2 Classification based on the pests controlled

Pesticides are classified based on the pests controlled into:

- Insecticides: act on insects.
- Algaecides: control the growth of algae.
- Herbicides: control weeds.
- Bactericides: act on bacteria.
- Fungicides: act on fungi.
- Rodenticides: control rodents.
- Larvicides: Inhibit the growth of larvae.
- Repellants: Repel pests by their taste or smell.
- Desiccants: Act on plants by drying their tissues.
- Ovicides: Inhibit the growth of eggs of insects and mites.
- Virucides: Act against viruses.
- Avicides: kill birds.
- Nematicides: Kill nematodes that act as parasites of plants

3.2.3 Classification of pesticides based on how biodegradable they are:

- i) Biodegradable pesticides: The biodegradable kind is those which can be broken down by microbes and other living organisms into harmless compounds'
- ii) Persistent pesticides: These are pesticides which may take months or years to break down.

Another way to classify pesticides is the consideration of their chemical forms or those derived from a common source or production method

Chemically related pesticides

- i) Organophosphates: Most organophosphates are insecticides; they affect the nervous system by disrupting the enzyme that regulates a neurotransmitter.
- ii) Carbonates: Similar to the organophosphorus pesticides, the carbonate pesticides also affect the nervous system by disrupting an enzyme that regulates the neurotransmitter. However, the enzyme effects are usually reversible
- iii) Organochlorine insecticides: They were commonly used in the past but now many countries have removed organochlorine

- insecticides from their market due to health and environmental effect and their persistent nature, eg DDT, Chloradane and Toxaphene
- iv) Prethroid: These are a synthetic version of pyrethroid, a naturally occurring pesticides found in chrysanthemums (flower). They were developed in a way so as to maximize their stability in the environment.
 - v) Sulfonylurea herbicides: These have been commercialized for weed control such as pyrethroid-sodium, cyclosulfamtrion etc.

3.3 Production of Pesticides

Pesticide production involves at least three separate activities. The active ingredient is first synthesized in a chemical factory, then formulated in the same place or sent to a formulator, who prepares the liquid or powder form. The pesticide is then sent to the farmer or other certified applicator, who dilutes it before applying it to the fields.

3.3.1 Synthesizing the pesticide

When a new pesticide is first developed, it is manufactured on a small scale in a laboratory. If the substance proves viable, production begins in the factory. Batch or continuous manufacturing insures a high volume, perhaps as much as 500 kilograms per cycle. Synthesizing a pesticide is a complex chemical procedure that requires trained chemists and a large, sophisticated laboratory. The basic procedure entails altering an organic molecule to form a pesticide. This may involve any of a number of specific reagents and catalysts and often must take place in a controlled climate (e.g. within a certain temperature range). Once synthesized, the active ingredient is packaged and sent to a formulator. Liquid insecticides can be shipped in tank trucks or 200-liter drums. Transport of the active ingredient follows all regulations for hazardous materials transportation.

3.3.2 Formulating the pesticide

A formulator accepts the active ingredient, measures out the proper amount, mixes it with carrier if it is to be a liquid pesticide or with inert powders or dry fertilizers if it is to be a dust pesticide, then bottles or packages it. Liquid pesticides are packaged in 200-liter drums if a large-scale farmer is the anticipated customer or 20-liter jugs for small-scale operations. Dry formulations can be packaged in 5 to 10-kilogram plastic or plastic-lined bags. An emulsified formulation is usually concentrated to render transport easier (the active ingredient typically makes up 50 percent of the emulsified concentrate), but granulated and dry pesticides are ready to use. The pesticide might be stored a short

time before it is requested. When it is ready for transport, the estimated necessary amount is sent to the farmer, who dilutes the emulsified concentrate to create the amount of pesticide desired. In most instances, the final product consists of only 0.5 to 1 percent of the original active ingredient. The pesticide is now ready to be applied.

3.3.4 Applying the pesticide

There are several ways to apply a pesticide. The method with which Americans are most familiar is crop dusting, though its use is generally limited to large, flat areas. A plane loaded with 2000-liter (or larger) tanks flies over a field and sprays out the pesticide from booms. Booms are long, horizontal rods from which several sprinklers spray down. Another method is to attach the tanks and booms to a tractor and spray closer to the ground. For small farmers, the most economical method of spraying is to use one or more workers with hand-held sprayers attached to small tanks. A hand pump can be carried on the shoulder; its tank capacity is only about 3 to 12 liters. Small tanks with a capacity of around 200 liters are also used. The pesticides are applied with a hand gun. A rough estimate of the amount applied is 150 to 300 liters per hectare.

SELF-ASSESSMENT EXERCISE

- i. Give five examples each of chemical pesticides and biopesticides.
- ii. In a tabular form, mention ten pesticides and indicate the pest controlled by them.
- iii. Describe the production process of pesticides.

4.0 CONCLUSION

A pesticide is any substance or mixture of substances intended for preventing, destroying, repelling, or mitigating any pest. Though often misunderstood to refer only to insecticides, the term pesticide also applies to herbicides, fungicides, and various other substances used to control pests. Pesticide production involves at least three stages of first synthesizing active ingredient in a chemical factory, then formulated in the same place or sent to a formulator to be in liquid or powder form. The pesticide is then sent to the farmer or other certified applicator, who dilutes it before applying it to the fields. That is synthesizing, formulating and application.

5.0 SUMMARY

In this unit, you have learnt that:

Pesticides are products that destroy various agricultural pests, including weeds (herbicides), insects (Insecticides), bacteria (microbicides) and fungi (fungicides). They cause economic damage to crop or ornamental plants and are hazardous to the health of domestic animals or humans.

Pesticides can be classified based on their origin and the pests they control. Classification of pesticides based on how biodegradable they are biodegradable pesticides are those which can be broken down by microbes and other living organisms into harmless compounds. Persistent pesticides are pesticides which may take months or years to break down. Another way to classify pesticides is the consideration of their chemical forms or those derived from a common source or production method. Another way to classify pesticides is the consideration of their chemical forms or those derived from a common source or production method. Chemical related pesticides include organophosphates, carbonates, organochlorine insecticides, prethroid and sulfonylurea.

6.0 TUTOR-MARKED ASSIGNMENT

1. List the ingredients that can be used to make pesticides at home
2. Explain how to produce pesticides using local raw materials

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[Assessed March 12, 2020]

UNIT 2 DYES

3.2 Classification of Dyes

<https://www.youtube.com/watch?v=3wavGkZZDHk>

3.4 Dyeing Process-based dyes.

<https://www.youtube.com/watch?v=8R4lAladUj0>

3.5 Production Process of Dyes

<https://www.youtube.com/watch?v=itOf01gg7go>

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1.0 INTRODUCTION

Dyes industry plays an important role in the overall growth of chemical industry. The preparation and usage of dyes is one of the oldest forms of human activities. The first synthetic organic dye,

mauveine, was discovered by William Henry Perkin in 1856. Synthetic dyes are now available in several colours or shades are amongst the oldest chemicals produced by man. Dyes are now available in a wide variety of shades to meet the requirements of different shades in all materials. Textile, carpet and garment industries are the largest consumers of dyes. The growth of the textile industry has a direct impact on the growth of dyes industry.

2.0 OBJECTIVES

By the end of this unit, you should be able to:

- classify dyes based on source of materials, dyeing process, chromophore, application, nuclear structure and colour index.
- state the functions of chromophore and auxochrome.
- write short notes on the examples of dyes classified based on dyeing process.
- describe the production process of dyes.

3.0 MAIN CONTENT

3.1 Dyes

Dyes are coloured, ionizing and aromatic organic compounds which have affinity to the substrates to which they are being applied. Dyes are generally applied in an aqueous solution which may also require a mordant for improving the fastness of the material on which it is applied. Various hazardous waste stream is generated during manufacture of dyes and intermediates. Many dyes like azo dyes, benziidine dihydrochloride and benzidine based dyes have been banned in some parts of the world. The environmental pressure has necessitated changes in process Chemistry and technology and use of safer and eco-friendly raw materials.

3.2 Classification of Dyes

3.2.1 Based on source of materials

Dyes are classified based on the source from which it is made into natural dyes and synthetic dyes.

3.2.2 Based on Dyeing process

Dyes are classified based on dyeing process into acid dyes, basic dyes, direct or substantive dyes, vat dyes, fibre-reactive dyes, disperse dyes, azo dyes, mordant dyes, sulphur dyes etc.

3.2.3 Based on Chromophore

Dyes are classified based on nature of their chromophore into acridine dyes, anthraquinone dyes, azo dyes, diazonium dyes, arylmethane dyes, nitroso dyes, phthalocyanine dyes, azin dyes, indophenols dyes, oxazin dyes, oxazone dyes, thiazole dyes, thiazin dyes, fluorine dyes and rhodamine dyes etc.

3.2.4 Based on Application

Based on application, dyes are classified into food, cosmetics and drug dyes, laser dyes, leather dyes, solvent dyes, contrast dyes, carbine dyes etc.

3.2.5 Based on nuclear structure

Dyes according to their nuclear structure can be classified into cationic dyes and anionic dyes.

3.2.6 Based on colour index

Colour index is compendium of dyes where every colorant is assigned a generic name and a constitution number. Colour index recognizes twenty-six types of dyes by chemical classification.

3.3 Chromophore and Auxochrome

Dyes are basically ionizing and aromatic compounds containing chromophores which make the dyes proficient in their ability to absorb radiation. Auxochrome is a group of atoms attached to a chromophore. This is responsible for providing solubility and cohesiveness to dyes.

3.4 Dyeing Process-based dyes.

3.4.1 Acid dyes

Acid dyes are water-soluble anionic dyes and insoluble in acid bath. They are used for dyeing of wool, silk, nylon, acrylic fibre, paper and leather.

3.4.2 Basic dyes

Basic dyes are water-soluble cationic dyes. They are mostly amino and substituted amino compounds. Basic dyes are used for dyeing acrylic fibre, cotton, wool, paper.

3.4.3 Direct dyes

Direct dyes are used in a neutral or slightly alkaline dye bath without addition of mordant. They are used for dyeing cotton, wool, silk, paper and nylon. They are generally azo dyes.

3.4.4 Disperse dyes

Disperse dyes are used for dyeing synthetic fibres like cellulose acetate, polyesters, nylon and acrylic fibres. They are applied as finely divided materials in the presence of dispersing agent.

3.4.5 Vat dyes

Vat dyes have highly complex structures and are insoluble in water. They are used after reduction in alkaline liquor which produces water-soluble alkali salt.

3.4.6 Reactive dyes

Reactive dyes react to form covalent bond which directly react with the fibre and provide excellent wash resistance.

3.4.7 Mordant dyes

A mordant is a chemical that combines with the dye and fibre usually to improve the fastness of the dye. As the principal modern mordants are dichromates and chromium complexes, mordant dye usually means chrome dye. Most mordant dyes yield different colours with different mordants. They can be used with wool, wool blends, silk, cotton and certain modified-cellulose fibres.

3.4.8 Azoic dye

Azoic dyes are dyes that are not applied directly but are produced within the fibre itself. In azoic dyeing, colours are made on the fibre by coupling diazotized materials while in contact with fibre. Final colour is controlled by the choice of diazoic and coupling components.

3.4.9 Sulfur dyes

Sulphur dyes are most commonly used dyes manufactured for cotton in terms of volume. They are produced by reacting sulphide and polysulphides with chlorinated aromatics.

3.5 Production Process of Dyes

Dyes are synthesized in a reactor, filtered, dried and blended with other additives to produce the final product. The synthesis step involves reactions such as sulfonation, halogenation, amination, diazotization, and coupling, followed by separation processes that may include distillation, precipitation, and crystallization. In general, organic compounds such as naphthalene are reacted with an acid or an alkali along with an intermediate (such as a nitrating or a sulfonating compound) and a solvent to form a dye mixture. The dye is then separated from the mixture and purified. On completion of the manufacture of actual colour, finishing operations including drying, grinding, and standardization are performed. These are important for maintaining consistent product quality.

SELF-ASSESSMENT EXERCISE

- i. Classify dyes based on the following:
 - (a) Dyeing process
 - (b) Chromophore
 - (c) Source of materials
 - (d) Application
 - (e) Nuclear structure
- ii. Describe the production process of dyes.

4.0 CONCLUSION

A dye is a coloured substance that has an affinity to the substrate to which it is being applied. Apart from the dyeing process of dyes, there are several other ways to classify dyes.

5.0 SUMMARY

In this unit, you have learnt the following:

- Dyes are coloured, ionizing and aromatic organic compounds which has affinity to the substrate to which it is being applied. Many dyes like azo dyes, benziidine dihydrochloride and benzidine based dyes have been banned in some

parts of the world. Auxochromes- group of atoms attached to chromophores

- Dyes can be classified based on source of materials, dyeing process, chromophore, application, nuclear structure and colour index. Dyeing Process-based dyes include acid dyes, basic dyes, direct dyes, disperse dyes, vat dyes, reactive dyes, mordant dyes etc.
- The production process of dyes includes synthesizing in a reactor, filtered, dried and blended with other additives to produce the final product

6.0 TUTOR-MARKED ASSIGNMENT

Name some Nigerian local plants in your locality that contains dye

7.0 REFERENCES/FURTHER READING

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UNIT 3 FLAVOURING AGENTS

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- 1.0 Introduction
- 2.0 Intended Learning Outcomes
- 3.0 Main Content
 - 3.1 Flavouring Agents.
 - 3.1.1 Taste
 - 3.1.2 Odour
 - 3.1.3 Feeling factor
 - 3.2 Types of Flavouring agents
 - 3.2.1 Natural Flavouring agents
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 - 3.3 Production of Flavouring agents
 - 3.3.1 Benzaldehyde
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 - 3.3.4 Monosodium Glutamate (MSG)
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- 6.0 Tutor-Marked Assignment
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1.0 INTRODUCTION

Flavour refers to a mixed sensation of taste, touch, smell, sight and sound. With the expansion of technology in the flavour industry, many artificial or imitation flavours have been created. Cough syrups, laxatives, sedatives, antihistamines, antibiotics, vitamins and pediatric formulations are now available in a variety of flavours which successfully mask unpleasant tastes without affecting physical and chemical stability.

2.0 OBJECTIVES

By the end of this unit, you should be able to:

- State the two major types of flavouring agents.
- give examples of natural and synthetic flavouring agents.
- describe the commercial production process of some flavouring agents.

3.0 MAIN CONTENT

3.1 Flavouring Agents

Flavour is a complex effect of taste, odour, and feeling factor i.e., touch, sight, and sound, to produce physicochemical and psychological actions that influence the perception of a substance. There are four basic flavors which the nerve endings in the taste buds on the tongue can detect: sweet, sour, salty and bitter.

3.1.1 Taste

There is a close co-relationship between chemical structure and taste. Sour taste is due to acidic nature and lipid solubility of substance. Examples are lemon, vinegar, citric acid, malic acid, and apple. Salty taste is due to cationic species, halide salts. Examples are sodium chloride, sodium bromide and sodium iodide. Increase in molecular weight of halide results in increase in bitter taste. Examples are potassium bromide, ammonium salts. Sweet taste is due to polyhydroxy compounds and aqueous solubility. Examples are sugar, glycerin and alpha amino acids.

3.1.2 Odour

Odour is defined as ‘Taste from a distance’. It is very closely allied to taste. Odourous volatile substances generate vapors which interact with olfactory cells and elicit receptors. The brain receives impulses from a group of microscopic olfactory receptors in the nose which it co-ordinates with the gustatory stimuli to produce the mingled sensation that is recognized as the flavor of the substance.

3.1.3 Feeling factor

Feeling factor is a combination of sight, sound, and touch i.e. texture (soft/hard), viscosity, cooling/ warmth, irritation sensation, etc. For example, flavoured viscous multi-vitamin liquid gives mouth feel effect, menthol in mouthwash gives cooling effect.

3.2 Types of Flavouring agents

Flavours are combined with the sweetening agents like sucrose, sorbitol, invert syrup, saccharine, etc. to enhance the flavouring effect. There are two major types:

- Natural flavouring agents
- Artificial flavouring agents

3.2.1 Natural Flavoring agents

Volatile oils such as anise, caraway, cinnamon, clove, dill, ginger, lemon, orange and peppermint are used as flavouring agents in a variety of forms. The vehicles of mixtures are often aromatic waters while alcoholic or hydro alcoholic solutions of oils (tinctures or spirits) provide convenient concentrated preparations for flavouring purposes (lemon, peppermint and compound orange spirits, and strong ginger tincture are examples). Flavours containing aromatic oils (except lemon and orange) are more suitable than fruit syrups for neutral preparations. Fruit flavours are prepared from fruit juices, peel of citrus fruits. Lemon and orange oils keep badly and develop an unpleasant turpentine-like taste. By removing most of the terpenes, terpeneless oils are produced which, compared with the natural oils, are about 20 times stronger in flavour and odour, are more readily soluble and have better stability.

For solid dosage form, vanillin crystals and dried lemon extract are used. For liquid dosage form, alcoholic, aqueous and hydro alcoholics (tinctures or spirits) are used.

3.2.2 Synthetic Flavouring agents

These are prepared by chemical reactions. In addition to synthetic sweeteners, other synthetic chemicals are used in flavouring. These are often preferred to natural materials because of their more constant composition, more ready availability, lower cost, greater stability, and more predictable incompatibilities. For example, esters (methylsalicylate), aldehydes (synthetic vanillin, benzaldehyde, and cinnamaldehyde), fatty alcohols, ketones, lactones and alcohols are used. Chloroform has an agreeable, warm, sweet taste and is used as a vehicle Chloroform water BP. For emulsified products, soft flavours like benzaldehyde and vanillin are most suitable. Benzaldehyde has the odour of bitter almonds and is a substitute for wild cherry syrup and volatile bitter almond oil. Benzaldehyde provides the odour and flavor of fresh almonds. Cinnamaldehyde is the oil of cinnamon and vanillin is the main flavouring agent of vanilla beans. Vanillin is useful when, as with liquid paraffin emulsions, the medicament has bland taste. Fractionated coconut oil, a non-aqueous vehicle for oral preparations, is difficult to flavour because of its oily nature; imitation ground almond oil and olive oil are suitable flavors.

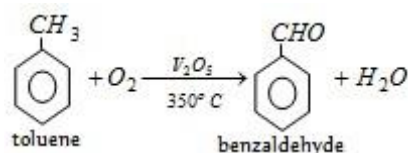
The esters of ethyl, methyl, amyl, propyl, and benzyl alcohols with acetic, propionic, butyric, salicylic, caproic, formic, valeric and anthranilic acids are widely used to characterize fruit flavors. Anethole has the taste of anise and licorice, benzyl acetate tastes like raspberry or

cherry, and allylcaproate is used for pineapple flavors. Other common compounds used for flavourings are diacetyl (butter), menthol (mint) and isoamyl acetate (banana).

3.3 Production of Flavoring agents

3.3.1 Benzaldehyde

Commercially, benzaldehyde is produced by several methods and in two grades, technical and refined. The refined chlorine-free grade is required for flavoring use and it is economically produced by the direct vapor-phase oxidation of toluene. However, this oxidation is sometimes carried out in the liquid phase.



Commercially, the oxidation of toluene is done with air and diluted with nitrogen (to prevent complete oxidation) at 500^o C in the presence of oxides of Mn, Mo or Zr as catalyst. Benzaldehyde can also be produced commercially by oxidation of benzyl alcohol. This involves the treatment of benzyl alcohol with dil. HNO₃ or acidic potassium dichromate or chromic anhydride in acetic anhydride or with copper catalyst at 350^o C.

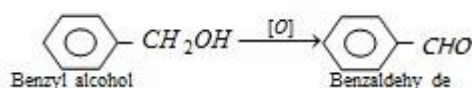


Fig 10 a and b: Benzaldehyde production

3.3.2 Vanillin

Vanillin is the main flavoring agent of vanilla bean which is the immature fruit of the orchid *Vanilla planifolia*. The pods are picked when they are just starting to turn from a uniform green to yellow at the tip and have a rather disagreeable odor. The green pods undergo a curing treatment of from 3 to 5 months' duration. The cured bean is pliant, shaky and dark-colored. The odor has become full and rich and the treatment may have left white aromatic crystals on the outside of the bean. This is because, the glucoside glucovanillin present in the bean, has been acted upon by a ferment and split into glucose, vanillin, and other aromatics. Substances identified in the vanilla bean are anisic acid, alcohol, and aldehyde; vanillic acid and alcohol; cinnamic acid and its esters; vanillin, ethyl vanillin, and possibly other homologs of vanillin.

As of 2001, the annual demand for vanillin was 12,000 tons, but only 1,800 tons of natural vanillin was produced. The remainder was produced by chemical synthesis. As of today, most vanillin is produced from the petrochemical raw material guaiacol. Several routes exist for synthesizing vanillin from guaiacol.

At present, the most significant of these is the two-step process practiced by Rhodia since the 1970s, in which guaiacol (**1**) reacts with glyoxylic acid by electrophilic aromatic substitution. The resulting vanillylmandelic acid (**2**) is then converted via 4-Hydroxy-3-methoxyphenylglyoxylic acid (**3**) to vanillin (**4**) by oxidative decarboxylation.

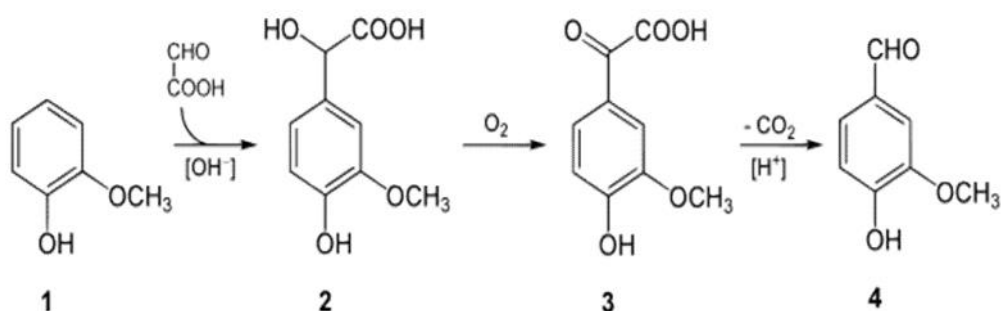


Fig 11: Vanilla production

3.3.3 Natural Fruit Concentrates

Because of the large percentage of water in most common fruits and the presence of considerable amounts of sugar and other easily fermented materials, special processes are employed in handling fruit flavors. Such processes include:

3.3.3.1 Distillation and Extraction of the fruit

The ripe fruit is stoned and comminuted. It is then subjected to steam distillation and rectification until the entire aroma is concentrated in a small portion of the aqueous distillate. This portion is then extracted with low-boiling petroleum ether, and the ether removed under vacuum to leave an essence, or quintessence, of the fruit used. Cherry, apple, strawberry and raspberry are treated by this method.

3.3.3.2 Extraction of the juice

The expressed and filtered juice is extracted directly without previous distillation. Occasionally, the juice is allowed to ferment slightly before extraction. This is supposed to result in a fuller flavor.

3.3.3.3 Concentration of the juice

The expressed and filtered juice is concentrated in vacuum evaporators with a low degree of heat until the water is largely driven off and the sugar concentration is high enough to inhibit bacterial growth. This type of concentrate often has a “jam” or cooked flavor, especially in the case of the strawberries. An alternative method of concentration is freezing. After reducing the temperature sufficiently, the mush of practically pure water ice is filtered off, and the partly concentrated juice is refrozen and refiltered until the requisite strength is obtained. This is the optimum method of producing concentrates, since there is little injury from heat, and the slight off-flavors from oxidation can be avoided by running the process in an atmosphere of carbon dioxide.

3.3.4 Monosodium Glutamate (MSG)

This compound is an important flavouring agent, yet has no flavour of its own. It accentuates the hidden flavours of food in which it is used. Glutamic acid exists in three forms, but only the monosodium salt of L-glutamic acid has a flavor-accentuating capacity. Previously, it was made by hydrolysis of wheat gluten, which contains about 25% glutamic acid, but presently, it is mostly made by submerged bacterial fermentation of carbohydrates. More and more important constituents of flavours are being made by the usual chemical synthetic procedures. Some constituents are chemically synthesized from an isolate or other natural starting material and are classified as semi synthetics.

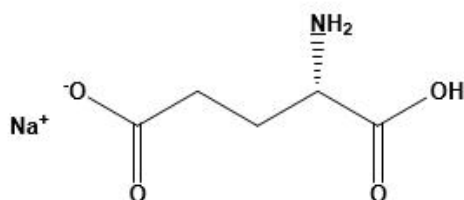


Fig 12: Monosodium glutamate

3.3.5 Benzyl benzoate

Benzyl benzoate has a faint aromatic odor, boils at 323 to 324°C and is a flavouring material. It occurs naturally in balsams but is prepared commercially by the esterification of benzoic acid with benzyl alcohol or by the Cannizzaro reaction with benzaldehyde

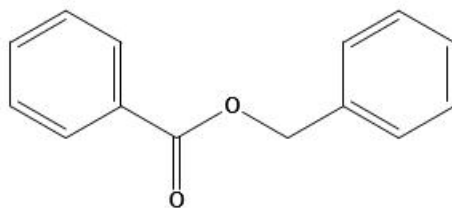


Fig 13: Benzyl benzoate

3.3.6 Methyl salicylate

Methyl salicylate (an ester of salicylic acid) is a very important ingredient in the flavouring industries. It is prepared as follows: Carbon dioxide and sodium phenate are reacted under pressure to obtain the salt of phenyl carbonic acid. This salt is isomerized to sodium salicylate by heating from 120 to 140°C. The ester is made from the acid and alcohol.

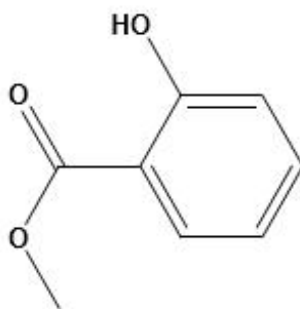


Fig 14: Methyl Salicylate

SELF-ASSESSMENT EXERCISES

- i. Write notes on natural and synthetic flavoring agents.
- ii. Describe the production processes of the following flavoring agents:
 - (a) Benzaldehyde
 - (b) Vanillin
 - (c) Benzyl benzoate
 - (d) Methyl salicylate
 - (e) Monosodium Glutamate (MSG)

4.0 CONCLUSION

Flavourings are prepared from essential oils, such as almond and lemon; from vanilla; from fresh fruits by expression; from ginger by extraction; from mixtures of essential oils and synthetic organic chemicals; or entirely from synthetic chemicals, with alcohol, glycerol, and propylene

glycol, alone or in combination, as solvents. Certain synthetic organic chemicals lend a distinctive note to imitation flavorings—for example, benzaldehyde to almond and benzyl butyrate to raspberry.

5.0 SUMMARY

In this unit, you have learnt the following:

- Flavor is a complex effect of taste, odour, and feeling factor i.e., touch, sight, and sound, to produce physicochemical and psychological actions that influence the perception of a substance.
- Cough syrups, laxatives, sedatives, antihistamines, antibiotics, vitamins and pediatric formulations are now available in a variety of flavours
- There are four basic flavors which the nerve endings in the taste buds on the tongue can detect: sweet, sour, salty and bitter. Two major types flavouring agents include natural flavouring agents and artificial flavouring agents. Vanillin is the main flavoring agent of vanilla bean and there is commercial production of some flavoring agents. Commercial benzaldehyde is produced by several methods and in two grades, technical and refined.

6.0 TUTOR-MARKED ASSIGNMENT

Mention all local but natural food flavouring agents in Nigeria you know.

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UNIT 4 EXPLOSIVES

3.3 Characteristics of Explosives

https://www.youtube.com/watch?v=p694_czdTMY

3.4.1 Nitrocellulose Production Process

https://www.youtube.com/watch?v=CmgrkAUjq_4

3.4.2 TNT Production Process

<https://www.youtube.com/watch?v=0J2flEqJvWI>

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- 1.0 Introduction
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 - 3.2.2 High Explosives
 - 3.2.3 Primary explosives
 - 3.2.4 Secondary explosives
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 - 3.3.4 Fume Characteristics
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1.0 INTRODUCTION

An explosive is a chemical compound or mixture which when exploded by action of heat or impact gives large volume of gases in a very short time at high temperature and pressure. All commercial explosives are broadly divided into two categories: low explosives and high explosives.

2.0 OBJECTIVES

By the end of this unit, you should be able to:

- classify explosives.
- give examples of explosives.
- explain the characteristics of explosives.
- describe nitrocellulose and TNT production processes.
- enumerate the applications of explosives.

3.0 MAIN CONTENT

3.1 Explosives

Explosives are materials that decompose rapidly and spontaneously with the evolution of large amounts of heat and gas, under the influence of thermal or mechanical shock. Explosives contain a great amount of potential energy that can produce an explosion if released suddenly, usually accompanied by the production of light, heat, sound and pressure. Commercial explosives usually have detonation velocities.

3.2 Classification of Explosives

Explosives can be basically classified according to velocity and sensitivity.

3.2.1 According to Velocity

3.2.1.1 Low Explosives

Low explosives burn at a slower rate and create less pressure. They are normally used as propellants to send a rocket into space or force a bullet out of a gun. Usually, low explosives have combustible substances, an oxidant that burns at speeds ranging from a few cm/sec to 400 m/sec, but usually on the lower end of that scale. Low explosives combine together a combustible substance and an oxidant at sufficient temperature releasing heat and rapidly expanding gases. The chemical reaction in low explosives is called deflagration which is a rapid process of combustion without accompanying any shock wave but gives a heaving effect. Common examples of low explosives are gum powder, black powder and nitrocellulose.

3.2.1.2 High Explosives

High explosives are chemicals that explode faster than the speed of sound. They burn more rapidly and create more pressure compared to low explosives. They detonate instantaneously, i.e. reactions in high explosives are characterized by an associated shock wave initiated by a detonator. There are many reaction sequences involved in a detonation process. It involves combination of a metal with chlorine releasing excess energy in the process. Other reactant combinations include hydrogen with chlorine, metal with oxygen, hydrogen with oxygen, carbon with oxygen, oxygen with carbon monoxide, and nitrogen with hydrogen. Examples of high explosives include Nitroglycerine, 2, 4, 6,-trinitrotoluene (TNT) and dynamite.

3.2.2 According to Sensitivity

3.2.2.1 Primary explosives

Sensitive materials that can be exploded by a relatively small amount of heat or pressure are primary explosives.

3.2.2.2 Secondary explosives

Materials that remain relatively insensitive are secondary explosives.

3.3 Characteristics of explosives

The various characteristics of explosives include the following:

3.3.1 Velocity of detonation

It is the speed at which detonation wave travels through the media and it depends upon the explosive type. Average velocity of detonation varies from 2500 m/s to 5800 m/s.

3.3.2 Weight strength

Weight strength is the energy generated by an explosive relative to that produced by an equal weight of 94 AN 6 FO (94 %) Fuel oil.

3.3.3 Water Resistance

Explosives differ widely in resistance to water and moisture penetration. Some explosives deteriorate rapidly under wet conditions but others are designed to withstand water for long periods.

3.3.4 Fume Characteristics

Explosives when used under stipulated ventilation conditions should liberate a minimum of harmful gases in the products of detonation.

3.3.5 Thermal stability

Explosives compositions should be such that it will be stable under all normal conditions of usage.

3.4 Production of explosives

3.4.1 Nitrocellulose Production Process

Nitrocellulose is produced by causing cellulose to react with nitrating acid (a mixture of nitric acid and sulfuric acid). After nitration, centrifuges separate the nitrocellulose from the spent nitrating acid used in excess quantities. This spent nitrating acid is separated into nitric acid, sulfuric acid and water, and completely recycled back into the process. The next stage is the pre-stabilization stage where the nitrocellulose is washed with water, thus separating off any acid left on the fibres. Next, the viscosity of the nitrocellulose is adjusted by pressure boiling (heating under pressure to temperatures above 100°C).

The next stage is the post-stabilization stage where the nitrocellulose is washed with water and heated to temperatures below 100°C. The water is subsequently separated off to leave water content of 35%. This water-wet nitrocellulose can then be packaged

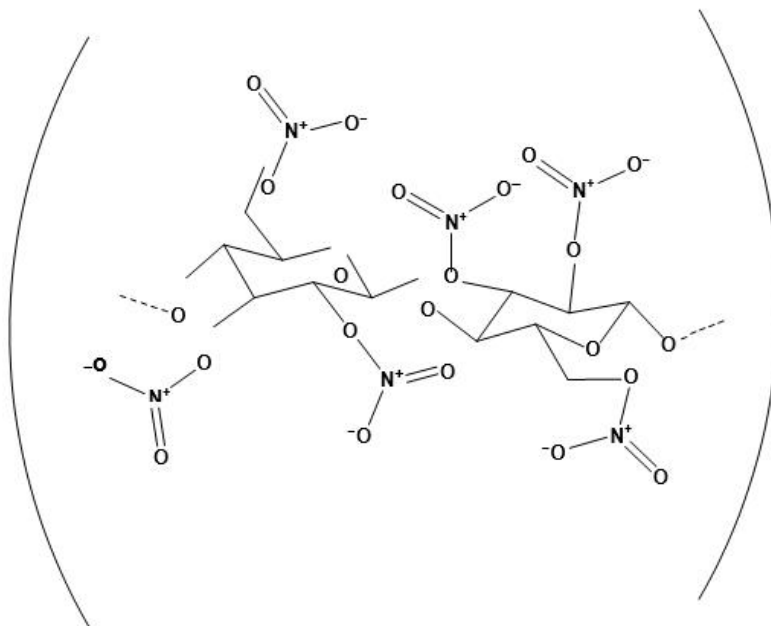


Fig 15: Nitrocellulose



3.4.2 TNT Production Process

The TNT production process is based on the known reaction of toluene direct nitration with nitric acid in the presence of sulphuric acid. The process depends gradually on a series of reactors. The TNT plant is provided as a continuous line starting from the raw materials feeding up to the final drying, flaking and packing. It is highly automated; thus the process runs automatically. The main process phases are Raw materials feeding; Nitration; Purification; Drying; Flaking; Packing.

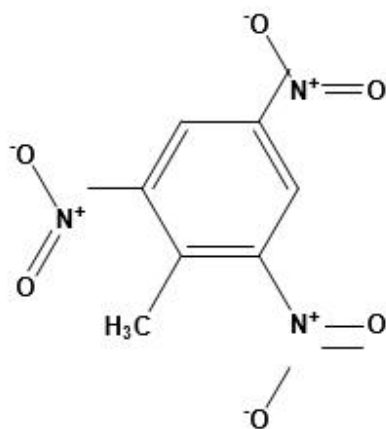


Fig 16: Trinitrotoluene

3.5 Applications of Explosives

The major use of explosives has been in warfare. High explosives have been used in bombs, explosive shells, torpedoes, and missile warheads. Non-detonating explosives, e.g., gunpowder and the smokeless powders, have found extensive use as propellants for bullets and artillery shells. The most important peaceful use of detonating explosives is to break rocks in mining. A hole is drilled in the rock and filled with any of a variety of high explosives; the high explosive is then detonated, either electrically or with a special high-explosive cord. Special explosives, called permissible explosives, must be used in coal mines.

These explosives produce little or no flame and explode at low temperatures to prevent secondary explosions of mine gases and dust. One important explosive used in mining, called ANFO, is a mixture of ammonium nitrate and fuel oil. Its use has revolutionized certain aspects of open-pit and underground mining because of its low cost and relative safety.

SELF-ASSESSMENT EXERCISE

- i. What are explosives?
- ii. Write briefly on the classification of explosives.
- iii. What are the characteristics of explosives?
- iv. Give five applications of explosives.

4.0 CONCLUSION

An explosive is a reactive substance that contains a great amount of potential energy that can produce an explosion if released suddenly. It is usually accompanied by the production of light, heat, sound, and pressure.

5.0 SUMMARY

In this unit, you have learnt the following:

- Explosives can be basically classified according to velocity and sensitivity.
- Explosives contain a great amount of potential energy that can produce an explosion
- Average velocity of detonation varies from 2500 m/s to 5800 m/s.
- According to velocity, explosives are classified as low and high.
- According to sensitivity, explosives are classified as primary and secondary.

- Explosives are classified according to velocity (low and high explosives), according to sensitivity (primary and secondary explosives). Explosives differ widely in resistance to water and moisture penetration. Explosives under stipulated ventilation conditions liberate minimum harmful gases on detonation. They are thermally stable under all normal conditions of usage. Explosives are produced by nitrocellulose production process and TNT production process. Applications of explosives are mainly in warfare. High explosives have been used in bombs, explosive shells, torpedoes, and missile warheads. Non-detonating explosives e.g. gunpowder and the smokeless powders have found extensive use as propellants for bullets and artillery shells. The most important peaceful use of detonating explosives is to break rocks in mining.

6.0 TUTOR-MARKED ASSIGNMENT

Discuss the production process of explosives.

7.0 REFERENCES/FURTHER READING

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UNIT 5 ADHESIVES

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 - 3.3.3 Vegetable-based adhesives.
 - 3.3.4 Solvent-based adhesives
 - 3.3.5 Reactive adhesives
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1.0 INTRODUCTION

Adhesive is a substance used for sticking two unlike bodies together due to molecular forces existing in the area of contact. All adhesives either contain polymers or polymers are formed within the adhesive bond. The development of adhesives has continued over the centuries to meet the requirements of various civilizations but it was not until the industrial revolution that demands were made for major advances in adhesive technology.

2.0 OBJECTIVES

By the end of this unit, you should be able to:

- give the meaning of adhesive.
- state the two types of adhesive.
- explain the production process of various adhesives.
- give the uses of adhesives

3.0 MAIN CONTENT

3.1 Adhesives

An adhesive is any substance applied to the surfaces of materials that binds them together and resists separation. The term “adhesive” may be used interchangeably with “glue”. Adhesives may be found naturally or produced synthetically.

The four main requirements for a material to perform as an adhesive include:

- It must “wet” the surfaces. This means the material must flow over the surfaces being bonded.
- It must adhere to the surfaces. This means the material must stay in position.
- It must develop strength. This means the material must become strong.
- It must remain stable. This means the material must remain unaffected by external conditions as long as the bond is required.

3.2 Types of adhesives

The two main types of adhesives are natural and synthetic.

3.2.1 Natural adhesives

Natural adhesives come from a variety of animal and vegetable sources. A major type of natural adhesive is animal glue. The animal glues are made from collagen, a protein found in skin, bone, and sinew. Natural adhesives have been in use since ancient times, particularly animal glue, casein glue, and adhesives made from plant resins. Beeswax and pitch were used as adhesives for centuries. Some 3,300 years ago, the ancient Egyptians used animal glue to build furniture, covering it with fine ornamental wood veneers and ivory.

3.2.2 Synthetic adhesives

Synthetic adhesives are compounded from simple chemicals. The main classes of synthetic adhesives are:

- Water-based adhesives
- Solvent-based adhesives
- Reactive adhesives
- Sealants

3.3 Production of adhesives

The production process of adhesives involves the combination of various substances in a homogeneous mix to form final products which are then packaged in a variety of containers.

3.3.1 Water-based adhesives

The raw materials used in the manufacture of water-based adhesives include polymer emulsions, polymers, plasticizers, preservatives and fillers. A fine polymer dispersion is formed by high intensity mixing of the polymer in water. The polymer emulsions are blended with other components in stirred mixers. Some operations will involve chemical reactions.

3.3.2 Hot-melt adhesives

Hot-melt adhesives comprise solid material requiring high temperature and application. The raw materials used include polymers, fillers and anti-oxidants.

3.3.3 Vegetable-based adhesives.

Cellulose is reacted with methyl chloride at high temperatures and pressures. The resultant product is normally a flaky solid. Biocidal agents are added to the product before packing.

3.3.4 Solvent-based adhesives

A natural or synthetic rubber or polymer is mixed with organic solvent and additives in a closed mixing vessel to form a homogeneous product.

3.3.5 Reactive adhesives

Reactive adhesives are manufactured as two-part systems, resin and hardener, which are packed separately and mixed before use. Epoxy resins are manufactured by the reaction of bisphenol-A and epichlorohydrin in a stirred reaction vessel. The vessel is heated and sodium hydroxide is added. The epoxy resin formed by the reaction is filtered off, further purified by solvent distillation and then mixed with the required additives and packaged.

3.3.6 Sealants

The required raw materials are weighed and then added to a mixing vessel where the ingredients are batch mixed. The product is then discharged for packaging, which may be automatic or semi-automatic.

3.4 Modern types of Adhesives

- 1) Anaerobic: These adhesives cure when in contact with metal and air is excluded eg when a bolt is home in a thread. They are often known as “Locking compounds”, they are used to secure, seal and retain tamed, threaded or similarly close fitting parts. They are based on synthetic acrylic resins
- 2) Cyanoacrylates: These adhesives cure through reaction with moisture held on the surface to be bonded. They need close fitting joints and usually solidify in seconds. They are suited to small plastic parts and to rubber. They are special type of acrylic resin
- 3) Toughened Acrylics: They are fast curing and offer high strength and toughens. Both one and two parts systems are available. In two parts system, no mixing is required because the adhesive is applied one substrate the activation to second substrate and the substrate joined. They tolerate minimal surface preparation and bond well to a wide range of materials.
- 4) Epoxies: These consist of an epoxy resin plus a hardener. They allow great versatility in formulation since there are many resins and many different hardeners. These materials have good strength, do not produce volatiles during curing and have low shrinkage properties.
- 5) Polyurethanes: They are chemically reactive formulations that may be one or two parts system and usually fast curing
- 6) Silicones: These are not very strong adhesives but are known for their flexibility and high temperature resistance
- 7) Phenolics: Phenolics are the first adhesives for metals and have a long history of successful use for joining metal to metal and metal to wood. They require heat and pressure for curing process
- 8) Polyimides: These are based on synthetic organic chains. They are available as liquids or films but are expensive and difficult to handle
- 9) Platisols: They are modified PVC dispersions that require heat to harden
- 10) Polyvinyl Acetate (PVA): This is the principal constituent of the PVA emulsion adhesives
- 11) Pressure- Sensitive Adhesives: These are suited for use as tapes and labels, although they do not solidify, they are often able to withstand adverse environments

3.4 Common adhesives and their uses

	Adhesive type	Uses
1	Animal glue	Binding of abrasives in sandpaper and other
2	Casein	Labels on beer bottles that do not come off in ice
3	Starch	Corrugated cardboard bonding
4	Natural rubber	Self-adhesive envelopes and other pressure-sensitive adhesives; adhesives that
5	Butyl rubber/Isobutylene	Additive for hot-melt adhesives, window sealants,
6	Amino resins	Bonding of layers in plywood and the bonding of
7	Polyurethane	Bonding soles to the bodies of shoes; also used in
8	Polyvinyl acetate	Book bindings and labels
9	Polyolefin	Hot melts
10	Acrylates or anaerobic adhesives	Adhesive used to keep nuts tight on bolts, such as those within ATMs and heavy
11	Silicone	Bathtub and shower sealants; also many car applications, such as oil pans and head gaskets

SELF-ASSESSMENT EXERCISES

- List four classes of synthetic adhesives.
- State five uses of adhesives.
- Discuss the topic “production of adhesives”.

4.0 CONCLUSION

There are natural and synthetic adhesives. Adhesives are produced by combination of various substances in a homogeneous mix to form final products which are then packaged in a variety of containers such as water-based adhesives, hot-melt adhesives, vegetable-based adhesives, solvent-based adhesives, reactive adhesives and Sealants.

5.0 SUMMARY

In this unit, you have learnt that adhesives are any substance applied to the surfaces of materials that binds them together and resists separation and that all adhesives either contain polymers or polymers are formed within the adhesive bond. Requirements for a material to act as an adhesive include: Must “wet” the surfaces. It must adhere to the surfaces. It must develop strength. It must remain stable.

Modern types of adhesives include anaerobic, cyanoacrylates, toughened acrylics, epoxies, polyurethanes, silicones, phenolics, polyimides, plastisols, polyvinyl acetate (PVA) and pressure - sensitive adhesives.

Several uses include bonding soles to the bodies of shoes; also used food packaging, book bindings and labels, hot melts etc.

6.0 TUTOR-MARKED ASSIGNMENT

Write an essay on the importance of adhesives to the shoe and leather industry

7.0 REFERENCES/FURTHER READING

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