Thermal decomposition products of kynol and nomex with reference to structure and toxicity

Shaker H. El-Sherbini

New Jersey Institute of Technology

Follow this and additional works at: https://digitalcommons.njit.edu/theses

Recommended Citation
https://digitalcommons.njit.edu/theses/1455

This Thesis is brought to you for free and open access by the Theses and Dissertations at Digital Commons @ NJIT. It has been accepted for inclusion in Theses by an authorized administrator of Digital Commons @ NJIT. For more information, please contact digitalcommons@njit.edu.
Copyright Warning & Restrictions

The copyright law of the United States (Title 17, United States Code) governs the making of photocopies or other reproductions of copyrighted material.

Under certain conditions specified in the law, libraries and archives are authorized to furnish a photocopy or other reproduction. One of these specified conditions is that the photocopy or reproduction is not to be "used for any purpose other than private study, scholarship, or research." If a user makes a request for, or later uses, a photocopy or reproduction for purposes in excess of "fair use" that user may be liable for copyright infringement.

This institution reserves the right to refuse to accept a copying order if, in its judgment, fulfillment of the order would involve violation of copyright law.

Please Note: The author retains the copyright while the New Jersey Institute of Technology reserves the right to distribute this thesis or dissertation.

Printing note: If you do not wish to print this page, then select "Pages from: first page # to: last page #” on the print dialog screen.
The Van Houten library has removed some of the personal information and all signatures from the approval page and biographical sketches of theses and dissertations in order to protect the identity of NJIT graduates and faculty.
THERMAL DECOMPOSITION PRODUCTS OF KYNOL AND NOMEX WITH REFERENCE TO STRUCTURE AND TOXICITY

BY

SHAKER H. EL-SHERBINI

A THESIS PRESENTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF MASTER OF SCIENCE IN ENGINEERING SCIENCE AT NEW JERSEY INSTITUTE OF TECHNOLOGY

THIS THESIS IS TO BE USED ONLY WITH DUE REGARD TO RIGHTS OF THE AUTHOR. BIBLIOGRAPHICAL REFERENCES MAY BE NOTED, BUT PASSAGES MUST NOT BE COPIED WITHOUT PERMISSION OF THE COLLEGE AND WITHOUT CREDIT BEING GIVEN IN SUBSEQUENT WRITTEN OR PUBLISHED WORK.

Newark, New Jersey 1977
APPROVAL OF THESIS

FOR

DEPARTMENT OF CHEMISTRY

NEW JERSEY INSTITUTE OF TECHNOLOGY

BY

FACULTY COMMITTEE

APPROVED:

____________________________________

____________________________________

____________________________________

NEWARK, NEW JERSEY

MAY, 1977
ACKNOWLEDGEMENTS

The author acknowledges the advice, guidance and encouragement offered by Dr. B. Kebbekus. Her advice was very helpful to work out the gas chromatography problem and the analytical technique used.

The author wishes to thank Dr. G. Lei for his valuable advice on polymer structures and for his supporting samples.
ABSTRACT

The purpose of this investigation was to study the combustion products of KYNOL and NOMEX as a fire retardant fibers. From the quantitative analysis data of the combustion products, the polymer structure is discussed and the property of thermal stability is explained.

From the analysis of the combustion products, the toxicity indices for the two fibers are determined. It is found to be 0.1 for KYNOL and 0.71 for NOMEX. This can be interpreted to mean that, if one gram of KYNOL is decomposed and the combustion products were diffused in one cubic meter of air, the probability of dying for a man in that space after 30 minutes exposure is only 10 %, while that of NOMEX is 71 %.
# CONTENTS

Summary | 1
---|---
1. Introduction | 2
2. Toxicity of gases | 5
  2.1. Physiological and psychological effects of gases | 5
    2.1.1. Toxic effect from gases and thermal degradation products | 9
      2.1.1.1. Oxygen | 9
      2.1.1.2. Carbon monoxide | 10
      2.1.1.3. Carbon dioxide | 13
      2.1.1.4. Hydrogen cyanide | 13
      2.1.1.5. Aliphatic hydrocarbons | 13
      2.1.1.6. Aromatic hydrocarbons | 14
    2.1.2. Toxic effect from polymer fumes | 16
    2.1.3. Toxic effect from smoke | 17
2.2. Definitions and evaluation of toxicity | 19
  2.2.1. Definitions of toxicity | 19
    2.2.1.1. Acute toxicity | 20
      2.2.1.1.1. Lethality | 21
      2.2.1.1.2. Primary irritants | 21
      2.2.1.1.3. Sensitizing agents | 21
      2.2.1.1.4. Behavior effects | 22
    2.2.1.2. Subacute toxicity | 22
2.2.1.3. Chronic toxicity.  
2.2.2. Evaluation of toxicity.  
3. Chemistry of polymer combustion.  
4. Aim of the work.  
5. Experimental.  
5.1. Material.  
5.1.1. KYNOL.  
5.1.2. NOMEX.  
5.2. Thermal decomposition.  
5.3. Analysis  
6. Results.  
6.1. Carbosieve column.  
6.2. Silicone column.  
6.3. Analysis of the combustion products of KYNOL fibers.  
6.3.1. Using the carbosieve column.  
6.3.2. Using the silicone column.  
6.3.3. Calculation of toxicity index for KYNOL.  
6.4. Analysis of the combustion products of NOMEX fibers.  
6.4.1. Using the carbosieve column.  
6.4.2. Using the silicone column.  
6.4.3. Calculation of toxicity index for NOMEX.  
7. Discussion.  
7.1. Structure and combustion.  
7.2. Combustion products and toxicity.
8. Conclusions.
9. References.

List of Tables

1. Signs and symptoms of toxicity of reduced levels of oxygen due to fire conditions.
2. Signs and symptoms at various concentrations of carboxy-hemoglobin.
3. KYNOL fiber-properties.
4. Retention times and response factors by using carbosieve column.
5. Retention times and response factors by using silicone column.
7. Combustion products analysis for KYNOL, using silicone column.
8. % of the combustion products of KYNOL.
9. Toxicity indices of the combustion products of KYNOL.
12. % of the combustion products of NOMEX. 52
13. Toxicity indices of the combustion products of NOMEX. 53
14. Maximum toxicity index. 59

List of Figures

1. Dose-Response curve for a chemical agent. 20
2. DTA thermogram for NOMEX. 35
3. Combustion apparatus. 37
4. KYNOL and NOMEX structures. 54
SUMMARY

Two types of fibers, namely KYNOL which is a phenolic cross-linked fiber, and NOMEX which is a poly-aromatic amide fiber, were thermally decomposed at 600°C. The combustion products were analysed using gas chromatography.

The quantitative analysis results were found to prove the polymer structure to a great extent, and also explain the thermal stability property of the two fibers. From the analysis of the combustion products, a toxicity index value has been determined, for KYNOL, it is 0.10 and for NOMEX 0.71; indicating a significantly greater toxicity for NOMEX.
1-INTRODUCTION

Historical Review on The Effect of Toxic Gases and their Smokes, Developed in Polymers during Pyrolysis or Combustion:

Toxic gases and vapors produced by oxidation and thermal decomposition reactions that occur during a fire are responsible for a large number of fire deaths. The potential danger of toxic combustion products may be increasing because of the increasing use of new materials, especially synthetic polymers, both as building materials and in goods and furnishings that make up the contents of buildings. Consequently, many fire authorities believe that some restrictions should apply to the use of materials that are capable of producing large amounts of toxic combustion products.

Work during the middle sixties at South-west Research Laboratories(34,49) indicated that obscured vision and toxicity of the smoke are two of the chief dangers. Recent articles in British and American fire journals suggest that except for clothing fires, more than half the deaths attributed to fire are caused by smoke rather than heat or actual burning(17).

Perhaps the first event focusing attention to the hazards of fire from a plastic material was the Cleveland Clinic fire in 1929(2) in which X-ray films, composed of the highly combustible nitrocellulose, caught fire and brought death to 125 persons. Analysis of the death pattern revealed that most of the deaths
were not due to the fire directly but were a consequence of the production of carbon monoxide and nitrogen oxides.

In the year of 1969 (39,40), reports from Europe, have shown that smoke damage often sharply increases the total property damage resulting from fires. In one instance, the combustion of 66 pounds of polyvinyl chloride caused a direct fire damage of $180,000. However the direct property loss due to corrosion by acids in the smoke was $4 million, and subsequent loss of profits was $9 million.

Over the past ten years from 1962 to 1972, more than 12,000 people have died each year as a result of fire involvement (32,33), due to toxic gases and smoke, more than flame and super heated air or oxygen depletion.

Numerous other fires in this country have also led to deaths not only due to the actual flames but to the gaseous products evolved from man-made materials. Not too surprising, however is the fact that research on toxicity aspects of pyrolysis products of man-made materials has lagged far behind the scientific and technical abilities to produce nearly unlimited polymer structures. Even a fair assessment of the toxic hazards cannot be adequately done at this time except in great generalities. The time, however, has passed for the toxic consequences to be ignored or to be minimized. Within the coming decade, newer polymeric materials and formulations will be increasingly utilized for low cost housing
and for practically all of the furnishing in these housing units.
Increase in man-made materials for all types of vehicles and clothing
will also intensify the need for toxicology data when and if these
materials are exposed to heat and fire.
2. TOXICITY OF GASES

2.1. Physiological and Psychological Effects of Gases.

The field of toxicology is no longer just concerned with the "poisonous" effect of a chemical agent or plant. Toxicology, in the modern version, utilizes a number of disciplines including pharmacology, pathology, histology, genetics and biophysics to delineate not only the gross effect which a chemical agent may produce in an animal or in a human but also to include the very subtle changes which may occur at the subcellular and cellular levels of an organism. It is important to become familiar with some of the classical aspects of toxicology, and for this reason, I shall give a short account in the next section.

With respect to animal testing studies, the work of Pryor and co-workers (35,36) is of fundamental importance in understanding the nature of the overall problem. In an early paper (33,35,36) Pryor defined the physiological effects of elevated temperature, oxygen depletion, carbon monoxide and carbon dioxide on man.

In a subsequent study, these authors studied the effect of two and more combined fire parameters on animal (36). The results of this work showed the presence of synergism for several of the investigated fire parameters (i.e., oxygen depletion, temperature, carbon monoxide and carbon dioxide).

In a real fire situation a number of factors will be responsible
for the death or serious incapacitation of persons in, or in the vicinity of, a fire. The more important of these factors may be listed as.

1- Direct consumption by the fire.
2- Extremely high temperatures.
3- Absence of oxygen.
4- Presence of carbon monoxide.
5- Presence of other gases.
6- Presence of smoke.
7- Development of fear.

From a toxicologic point of view, factors 3 to 6 become important considerations since factors 1 and 2 will bring about immediate death while factor 7 may or may not lead to death, depending upon whether a panic stricken person makes a rash decision such as jumping out of a window or heading directly into another danger zone (such as an oncoming vehicle or making contact with fallen power lines).

Exposure of humans to the various combustible and non-combustible gases as well as the particulates in smoke may bring about acute episodes of toxicity ranging from extremely minor irritant effects to death.

In real fire situations it becomes nearly impossible to ascertain which one or two agents (excluding absence of oxygen, presence of carbon monoxide and perhaps direct evidence of large quantities of particulate matter in the upper respiratory tract) caused death.
It becomes even more difficult, if not impossible, to ascertain the toxic potential of a specific material when it burns or is heated. Presently, the simplest approach is to have some knowledge of what gases are formed and to seek toxic information on the individual compounds if such knowledge is available. From this point on, the problem for the toxicologist becomes somewhat nightmarish since the combination of products being inhaled may not and generally does not produce the same biological response as when only one of the compounds is administered or inhaled. As is well known to the physician, a therapeutic effect of one drug may be appreciably enhanced or appreciably reduced when the patient has had a prior drug or when combinations of drugs are given to him. In the discussion to follow, it should be kept in mind that even though comments will be made in regard to toxicity it will probably be related to generally one compound or selected groups of compounds.

When an animal or man is placed in contact with a chemical agent, it can produce an acute toxic effect in a number of ways, perhaps the most important can be listed as follows:

1. The compound may act as a primary irritant upon the skin and/or mucous membranes.
2. The compound may be absorbed into the bloodstream leading to definite toxic symptoms and signs and progressing to death if the compound is not removed.
3- The compound may act as a sensitizing agent producing antibodies to the antigen. A repeated exposure to the same or nearly similar compound may produce from mild to very serious allergic manifestations.

4- The compound may be absorbed in very low concentrations producing no definite signs and symptoms of toxicity but may effect mental functions.

The first two can lead to rapid death during fire episodes due to the direct effect of the compound or, if not death, sufficient damage to cause hospitalization and treatment. The third (sensitizing agent) consequence has not received much attention in regard to fires but it should not be overlooked, at least in those cases where death does not occur or even in those instances in which no apparent harm is noted. An allergic response may, however, develop at another date but may have been initiated due to the fire or the heating of man-made materials. Finally, as has been indicated previously, low levels of compound may be sufficient to alter mental functions which will in turn lead to serious accidents or consequences for the person as well as for larger number of other persons.

With what has been said in this section kept in mind, some of the more important thermal degradation products will be reviewed. The comments will be brief for obvious reasons. Ideally, it would be suitable to categorize each of the compounds to be discussed according to some rating system for each of the potential consequences.
2.1.1. Toxic Effect from Gases and Thermal Degradation Products.

2.1.1.1. Oxygen. (2)

In this case, of course, the important factor is the absence of oxygen rather than the release of oxygen due to fire of heating of polymeric materials. Complete lack of oxygen will of course lead to death within a few minutes and lesser concentrations of oxygen in the air than normal will produce a number of signs and symptoms of hypoxia in persons exposed to that environment. Even if death does not occur due to no or low levels of oxygen in the immediate atmosphere, denial of sufficient oxygen to brain tissue for short periods of time will produce irreparable brain damage. Higher concentrations of oxygen but still below that considered as normal, will effect the brain cells in a reversible manner, but during this period the person will have behavioral changes which may produce faulty judgement leading to serious accidents and possible death or grave injuries to himself as well as to others. Some estimate has been made as to the signs and symptoms of toxicity of oxygen deficiency at various levels in the environment of a fire. These are shown in Table 1. and clearly indicate the rapid toxic effects which can develop when sudden decreases in oxygen levels take place in the ambient surroundings of a person exposed to a fire condition.
Table 1. Signs and Symptoms of Toxicity of Reduced Levels of Oxygen due to Fire Conditions. (2)

<table>
<thead>
<tr>
<th>Percent of Oxygen in air</th>
<th>Sign and Symptom</th>
</tr>
</thead>
<tbody>
<tr>
<td>20% or above</td>
<td>Normal</td>
</tr>
<tr>
<td>12 to 15%</td>
<td>Muscular coordination for skilled movements lost</td>
</tr>
<tr>
<td>10%</td>
<td>Consciousness continues but judgement is faulty and muscular effort leads to rapid fatigue.</td>
</tr>
<tr>
<td>6 to 8%</td>
<td>Collapse occurs quickly but rapid treatment would prevent fatal outcome.</td>
</tr>
<tr>
<td>6% or below</td>
<td>Death in 6 to 8 minutes.</td>
</tr>
</tbody>
</table>

2.1.1.2. Carbon Monoxide. (2)

Out of all the gases generated from the burning of a material (both natural and synthetic), the gas which produces the most deaths in real fire situations is carbon monoxide. Even though normal air has levels of carbon monoxide in parts per million, animals and man apparently can tolerate concentrations up to 100 ppm for short periods of time (up to eight hours) without any undue harm. Fire conditions, however, can release large concentrations of CO in
air and these levels can lead to death in very short periods of time. The main action of carbon monoxide after it is inhaled is to combine reversibly with hemoglobin (Hb) to form carboxyhemoglobin (CO-Hb). This reaction displaces oxygen in the blood and leads to anoxia and death if the reaction is not reversed. Carbon monoxide also interferes with oxygen release in the tissue but this appears to be of secondary importance as compared to combining with hemoglobin. Both animal and human studies have demonstrated that correlations can be made between signs and symptoms of toxicity and the percent CO-Hb formed. Table (2) summarizes this information and shows that concentrations below 10% produce no signs or symptoms. Most medical personnel and toxicologists agree that in general, most persons will not show toxic symptoms below a level of 20% carboxyhemoglobin. From this level on, however, extremely toxic manifestation will occur and death will be imminent in concentrations of 60% or more.

Table (2). Signs and Symptoms at Various Concentrations of Carboxyhemoglobin.

<table>
<thead>
<tr>
<th>% CO-Hb</th>
<th>Signs and Symptoms</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 - 10</td>
<td>No signs or symptoms.</td>
</tr>
<tr>
<td>10 - 20</td>
<td>Tightness across forehead, possible slight headache dilation of the cutaneous blood vessels.</td>
</tr>
</tbody>
</table>
In recent years attention has been given to possible toxic effects of carbon monoxide at levels where signs and symptoms of toxicity are not noted, as for example below 10% CO - Hb. Schulte (37) has explained this problem and has found that concentrations as low as 5% CO - Hb can effect certain psychomotor abilities. By applying the low rates to animal and human experiments, he came to the conclusion that low levels of carbon monoxide could have and most likely does have an effect upon judgment and situational decisions and responses.
2.1.1.3. Carbon Dioxide.

All fires will produce some levels of carbon dioxide which in turn may be inhaled by those in the vicinity of a fire. Since \( \text{CO}_2 \) is an important constituent of the body process, \( \text{CO}_2 \) is not considered as a toxic agent. Inhalation of carbon dioxide will however, stimulate respiration which in turn will increase inhalation of possible toxic components from the gases present from the fire. It is not correct to assume however, that toxic signs and symptoms will not occur in man. For example, inhaling \( \text{CO}_2 \) in concentrations of 10\% have caused in segments of test groups, headaches and dizziness as well as other symptoms. Higher concentrations (above 20\%) can lead to narcosis in animals and in most people. (2)

2.1.1.4. Hydrogen Cyanide.

Hydrogen Cyanide may be a lethal agent when ingested as a salt in a dose of less than 0.25 gram. Concentrations above 20 ppm in the air are considered as dangerous, possibly fatal. Initial inhalation of the vapors of HCN will cause a reflex stimulation of breathing which in turn will lead to greater concentration of gas entering the body. Within a very short time, the person becomes unconscious, and if not removed from the source, certain death will result. Cyanide will inactivate certain enzymes in the body and this will in turn prevent utilization of oxygen by tissue. (2)

2.1.1.5. Aliphatic Hydrocarbons.

Thermal degradation of all organic polymers will produce a
variety of aliphatic compounds having a range of molecular weights. The lower molecular weight compounds will produce narcosis in animals and man but as the series is ascended, the biological activity will decrease. With certain polymers there may be present unsaturated hydrocarbons when the polymer is degraded and these compounds will generally have a greater toxic effect than the saturated compound. In these mixtures there may also be present, acids, alcohols and aldehydes, each containing a toxic property.


2.1.1.6. Aromatic Hydrocarbons (2)

These compounds, starting with benzene and leading to other aromatic structures, will have both irritating properties as well as systemic toxicity. As the structures of the aromatic molecule is altered, the toxicity may be increased or decreased. Several of these aromatic compounds such as benzene will be absorbed not only by inhalation but by absorption through the skin. Levels of 100 ppm and above are considered dangerous to health.

Benzene (41): Acute human toxicity (from ingestion or inhalation), irritation of mucous membranes, restlessness, convulsions, excitement, depression. Death may follow from respiratory failure.

Chronic: bone marrow depression and aplasia; rarely, leukemia. Harmful amounts may be absorbed through skin.

Aniline (41): Intoxication may occur from inhalation, ingestion, or cutaneous absorption. Serious poisoning may result from ingestion of 0.25 ml. Acute toxicity: cyanosis, methemoglobinemia, vertigo, headache, mental confusion. Chronic: anemia anorexia, weight loss, cutaneous lesions. So-called aniline tumors of the urinary bladder are caused by intermediates in the manufacture of coal tar (aniline) dyes rather than by aniline itself.

Phenol (41): Ingestion of even small amounts may cause nausea, vomiting, circulatory collapse, tachypnea, paralysis, convulsions, coma, greenish or smoky-colored urine, necrosis of mouth and G.I. tract, icterus, death from respiratory failure, sometimes from cardiac arrest. Average fatal dose is 15 grams but death from 1.5 gram has been reported. Fatal poisoning may also occur by skin absorption following application to large areas. Chronic poisoning with renal and hepatic damage may occur from industrial contact.

o-Cresol (41): LD<sub>50</sub> orally in rats is 1.35 g/kg. Human toxicity the same as phenol.

p-Cresol (41): LD<sub>50</sub> orally in rats is 1.8 g/kg. Human toxicity the same as phenol.
2.1.2. Toxic Effects from Polymer "Fumes".

A number of years ago, it was found that certain heavy metals, when heated to high temperatures, released particulates which when inhaled by humans resulted in symptoms of illness such as dryness of the throat and dry coughs. In a number of cases the person would become nauseated and vomit. Surprisingly enough, in a few cases the symptoms abated within a day with no apparent ill effect to the person. The term metal fume fever was coined for this disease. A similar illness has now been recognized for Teflon, when this plastic is heated to high temperatures and similarly the signs and symptoms of toxicity abate after 24 hours (2). Harris was the first to report on "Polymer Fume Fever" in 1951 (19). Up to the present time, the exact mechanism for this type of toxic response has not been elucidated and still the only documented evidence of the illness is with Teflon, but it appears that other plastics having the same general properties of Teflon could also produce the symptoms. Unfortunately, as Zapp (51) has pointed out, similar results have not been duplicated in animals to permit sound scientific suggestions as to what the real causative mechanism is for the symptoms shown in man.
2.1.3. Toxic Effect from Smoke.

The term smoke is not always used or defined in the same manner and for this reason it will be defined here as follows (2,16). "The air borne products evolved when a material is decomposed by heat or burning. Smoke may contain gases, liquid or solid particles or any combination of these".

From what has been said it should be apparent that smoke may carry the various toxic compounds which were reviewed. To these however should be included particulate matter which can be inhaled. Depending upon the physical size of the agent it may be absorbed from lung tissue into the blood stream. In other cases, it may be trapped in lung tissue and either be phagocytized and removed (over a period of time) or it may be trapped in lung tissue and remain there indefinitely. Chronic effects of these "non-removed" particulates lodged in lung tissue over long periods could lead to malignant tissues as has been noted when persons have been exposed to various types of silicates and coal dust. Acute episodes of smoke inhalation can of course lead to suffocation due to the dense build up of smoke which prevent absorption of oxygen.

Smoke will cause hazards to life in an indirect manner. Development of fear in a person near fire can lead to acts which normally would not be executed, such as leaping from a building, or group fear can cause persons to attempt to escape a building through the same door resulting in entrapment of the people in the building.
Since smoke will also obliterate signs and reduce vision to such an extent that the person may never find the exit even though it is available to him, death or incapacitating injury then result.
2.2. Definitions and Evaluation of Toxicity.

2.2.1. Definitions of Toxicity.

Toxicology is the study of adverse effects of chemicals on various types of biological systems including man. This definition still holds, but in modern times the scope of toxicology has broadened that a more comprehensive definition is required. Perhaps the most suitable can be defined in the following manner (2).

"Untoward effects of any substance in the environment, including drug toxicities or poisoning, whether as a consequence of internal or external exposure, and relating to both immediate and long-term implications in the realm of human ecology, or to information which leads to an understanding of the mechanisms through which toxic manifestations arise and to the means for alleviation and control of toxic effects".

When an animal or human is exposed to a single chemical entity and depending upon the specific nature of the agent and the concentration, it may bring about a biological consequence at the site of contact (i.e. corrosive effect or in respiratory tract) or the chemical may enter the bloodstream through one or more orifices and produce a physiological, pathological or psychological response. The biological or psychological response will generally abate when the chemical is removed but again depending upon the specific chemical, the concentration, and the time of exposure the response may continue leading to irreversible damage and death.
Experimentally, the hazard or safety of a chemical is evaluated in animals utilizing three levels of studies. These include, 1. Acute toxicity, 2. Subacute toxicity and 3. Chronic toxicity. Each of these levels of studies will now be briefly reviewed.

2.2.1.1. Acute Toxicity.

The biological effect of a chemical agent when administered, ingested, inhaled or when applied to the skin in a single dose or concentration is generally regarded as falling under the broad category of "acute toxicity". Acute toxicity, however, can also apply to very short term exposures of animals and humans to chemical agents and in some instances to a limited number of administration or exposures as for example when a "sensitization test" is to be conducted. The toxicologist, however, places no rigid boundaries on the scope of tests or studies which he may choose to include under the category of acute toxicity. For our consideration we will include in this section brief accounts of acute toxicity under 1. Lethality, 2. Primary irritant, 3. Sensitizing agents and 4. Behavior effects.

![Dose-Response curve for a chemical agent](image-url)
2.2.1.1.1. Lethality.

As it appears from the sigmoid curve in Fig.1., it is most convenient to express the lethality of the test compound as the concentration or dose killing 50% of the animals is used to describe the acute toxic dose of a compound. This concentration is referred to as the LD$_{50}$ dose (lethal dose-50) when administered in a specific manner (oral, inhalation, injection, etc.).

The evaluation of the LD$_{50}$ in a number of a species of animals will be a fair guide to the acute lethal toxicity of the same compound in man.

2.2.1.1.2. Primary Irritants.

Acute toxicity evaluations should also include tests which will indicate the propensity of a compound to cause tissue irritation and damage. If the tissue response is severe it may lead to other toxic manifestations, as for example corneal damage and blindness or if the agent is extremely corrosive it may destroy tissue in the respiratory tract and in turn require surgical procedures to restore the tissue or organ to normal function if possible. Chemicals, which when applied to skin or mucous membranes and which lead to tissue alterations of one type or another, can generally be classified as primary irritants.

2.2.1.1.3. Sensitizing Agents.

It is important to distinguish between a substance acting as a primary irritant and one acting as a sensitizing agent. The primary irritant elicits its effect immediately on one application
while the sensitizing agent may show no primary irritation but when applied or injected may combine with a protein molecule and act as antigenic agent. This antigenic agent in turn will produce antibodies. Now if the compound is applied again or injected, an antigen-antibody reaction may occur leading to minor or to very serious allergic conditions which could lead to death or a crippling illness.

2.2.1.1.4. Behavior Effects.

The more important question here is what effect may the compound have on subjective symptoms in humans at dose levels much below those which can be measured by usual physiological means. In this case, the toxicologist must borrow techniques and experimental procedures from the experimental psychologist. The importance of behavior must become part of testing programs for chemical agents in particular for agents which enter the atmosphere such as air pollutants and agents released due to fires.

2.2.1.2. Subacute Toxicity.

It is defined as the cumulative effects of the compound can be ascertained as well as toxic effects upon various organs and tissues at dose levels which might originally have been judged to have a "no effect". For practical reasons, prolonged studies, on a new chemical agent is generally conducted up to three months. The term "subacute toxicity" is used for these prolonged studies (up to 3 months).
2.2.1.3. Chronic Toxicity.

It is now fairly well established that potential carcinogenic agents need to be administered to animals for very long periods of time (several years) to judge the compound as a carcinogenic agent. Chronic toxicity studies generally follow the procedures of the subacute toxicity study, but continue for a longer periods of time.
2.2.2. Evaluation of Toxicity.

Yoshio Tsuchiya and Kikuo Sumi in 1967 (45) suggested a method for evaluating the toxicity of combustion products from quantitative experimental data and literature data dealing with the lethal concentration of these products. The same authors in 1971 (46) discussed the possible use of the evaluation method in restricting materials based on their potential for producing large quantities of toxic gases at fires.

Toxicity, \( t \), due to a gaseous or volatile compound is assumed to be proportional to its concentration and to its relative toxicity

\[
t \propto C t_r
\]

Relative toxicity is defined as:

\[
t_r = \frac{1}{C_f}
\]

Where \( C_f \) is the concentration of gases fatal to man in 30 minutes exposure.

The toxicity of a decomposition product, based on both the nature of the compound and the quantity evolved, then becomes,

\[
t \propto \frac{C}{C_f}
\]

By comparing values of \( C/C_f \) for different decomposition products evolved under one set of conditions, toxicity from each product could be assessed. In order to present data on toxicity in a consistent manner, Tsuchiya and Sumi (46) suggest
using the equation,

\[ T = \frac{C_e}{C_f} \]

Where \( T \) is the toxicity index.

\( C_e \) is the concentration of volatile gaseous product evolved when one gram of original material is decomposed and the decomposition products are diffused in a volume of 1 m\(^3\).

Concentrations \( C_e \) and \( C_f \) are expressed in ppm. The toxicity index for a material is obtained from the sum of the toxicity indices of the combustion products. That is,

\[ T_t = \sum \frac{C_e}{C_f} \]

The toxicity index of a material depends on the experimental conditions under which the material is burned. The maximum value, \( T_m \), obtained from experimental data or derived from theoretical consideration provides a useful basis of comparison.

Values for \( C_f \), the concentrations of compounds that are fatal to man in a short exposure time of the order of 30 minutes, are available in the literature for a number of toxic compound that are produced at fires. There is a need for animal studies to establish \( C_f \) values of other compound and to reexamine some of the data that have been reported. When \( C_f \) is not found in the literature, an estimate often can be made for the compound from data on
similar compounds. For others, an estimate can be made from Threshold Limit Value (TLV)* that have been reported for large number of compounds (6).

* TLV; refers to airborne concentrations of substances and represents conditions under which it is believed that nearly all workers may be repeatedly exposed day after day without adverse effect, expressed as time-weighed concentrations for a 7 or 8 hour work day and 40 hour work week. Example; TLV for \( \text{SO}_2 \) is given as 5 ppm and 50 ppm for \( \text{NO}_2 \).
3. CHEMISTRY OF POLYMER COMBUSTION

A burning polymer is a complex combustion system. Fristrom (1974) has classified these reactions according to the phase (gas or condensed phase), also he has classified these reactions according to the thermal regime, since the temperature controls the chemistry (5,10,12,13,14,15,18,25,27,28,29,30,43,47,48).

As the thermal wave induced by combustion travels in the plastic, initially the temperature simply increases due to thermal conduction. Polymers are so high in molecular weight that they decompose before vaporization (14,29). If the polymer is pure and contains no free radicals, or dissolved oxidizer (e.g., O₂, NO₂), pure thermal initiation would require rupture of a C – C or C – X bond and processes would show high activation energy (50 – 100 k.cal/mole). Once initiated however the processes would proceed rapidly because of propagating chain reactions. Each ruptured bond produces two radicals which could react with low activation energy with other polymer chains. This can result in both depolymerization producing gaseous products and crosslinking which produces an involatile char. The relative amount of monomer obtained by pyrolysis is controlled by what is called the zip length which is defined as (29)

\[
\text{Zip length} = \frac{\text{Depropagation of monomer}}{\text{Termination + Transfer}}
\]
An example where depolymerization is dominant is polystyrene. The following quotation from Madorsky (29), outlines the process:

The most striking phenomenon in the thermal behaviour of poly α-methyl styrene is its almost complete conversion in the temperature range of 200 - 500°C into monomer. In the case of polystyrene, the presence of a phenyl group on every alternate carbon atom in the chain blocks to some extent the transfer of hydrogen in an intermolecular or in an intramolecular reaction at the site of a scission in the chain. As a result a considerable proportion of scissions result in the formation of a free-radical chain ends which proceed to unzip into monomer and dimer. The rest of scissions are accompanied by hydrogen transfer, resulting in one saturated and one unsaturated end, thus reducing the molecular weight of residual material. Fragments of a size larger than the dimer form from a further break down of the polymer chains. In the case of poly α-methyl styrene, in the pyrolysis below 500°C, hydrogen transfer is completely blocked from the sites of chain scissions by the presence, in addition to phenyl group, of CH₃ group in the α-position, and as a result the ends are in the form of free radicals which unzip into monomers. In pyrolysis at 800 and 1200°C considerable amounts of pyrolysis occur. This may be due to an escape of chain fragments, larger than a monomer, from the hot zone before they have time to unzip into monomers.
Formation of small molecular fragments, like $\text{H}_2$, $\text{CH}_4$, $\text{C}_2\text{H}_2$, $\text{C}_2\text{H}_4$ and $\text{C}_6\text{H}_6$ at 800° and 1200° is most likely a result of cracking of the monomer or of the larger fragment during their diffusion out from the sample and their passage through the hot zone of the apparatus (secondary reactions). As a result, the yield of monomer $\text{C}_9\text{H}_{10}$ at 1200° drops to 33.9% [29].

The mechanism of char formation involves crosslinking and also formation of conjugate double bonds followed by cyclization and then dehydrogenation. These reactions are generally the result of the elimination of a stable molecule such as water, one of the halogen acids or carbon monoxide.

In practice the rates of the multitude of possible reactions are often controlled by impurities and the previous history of the sample. Oxygen or other oxidizing impurities in the polymer can act as radical initiating sources and provide branching reactions. Ultraviolet light from sunlight and other radiation sources can initiate chain breaking and radical production which markedly lower the initiation. This is a factor in the aging of polymers [29]. These radicals have long life times because of the high viscosities of the polymers under normal conditions. Thus, one might expect that normal aged polymers would contain significant radical initiation sources from these mechanisms and be more susceptible to pyrolysis than carefully prepared virgin laboratory samples. If radical producing centers and foreign molecules
are present, extremely complex mixtures will be obtained even with pure thermal pyrolysis, in vacuo or in inert gas.

For more details, the following references discuss the mechanism of polymer combustion and pyrolysis:

(13, 25, 28, 29, 30, 43, 48).
4. AIM OF THE WORK

The aim of this work is to study the combustion products of two fire resistant fibers, KYNOL and NOMEX. The former is a phenolic cross-linked fiber and the latter is a poly-aromatic amide fiber.

The study of the combustion products was done by gas chromatography. From the quantitative analysis data, we will discuss the structure of the polymer, and also we will calculate the toxicity indices of the individual combustion products, and the total toxicity index of all the products for each polymer to figure out how dangerous it will be in case of fire.
5. EXPERIMENTAL

5.1. Material

5.1.1. KYNOL

It is a generic organic fiber derived from phenolic resin and available from The Carborundum Company under the trade mark KYNOL. It is described as a fiber which combines the required flame resistance and comfort properties.\(^{(8,9)}\)

Properties of KYNOL Fibers:\(^{(9)}\)

The fibers have been tested under a variety of flames ranging from a match to a torch and shown up to be non-melting and non-burning. Under these conditions the fibers carbonize showing excellent shape retention with little evolution of smoke or noxious gases. Other properties of KYNOL fiber are summarized in Table (3).

Table (3)

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tenacity (gms/denier)</td>
<td>1.7</td>
</tr>
<tr>
<td>Young's Modulus (gms/denier)</td>
<td>41</td>
</tr>
<tr>
<td>Elongation (%)</td>
<td>20</td>
</tr>
<tr>
<td>Specific gravity (gm/cm(^3)</td>
<td>1.25</td>
</tr>
<tr>
<td>Thermal conductivity (cal/sec/cm(^2\times)°C/cm)</td>
<td>(4.5 \times 10^{-4})</td>
</tr>
<tr>
<td>Dielectric strength (Volts/ml)</td>
<td>400</td>
</tr>
</tbody>
</table>
Behavior of KYNOL in a Flame (9):

The unusual flame resistance of KYNOL fiber in a Meker burner is compared to a roving of S glass. Within two seconds the sizing of S glass burns off and three seconds later the S glass roving has melted. KYNOL fiber on the other hand does not burn or melt but carbonizes and is self-supporting after one minute. Even under the stringent conditions of an oxyacetylene torch where temperatures may reach 2500°C, a KYNOL batt shows excellent resistance, the surface of the batt has formed a layer of carbon fibers which insulates the next layer as well as providing an effective black body surface for radiating away heat. Obviously the reason for KYNOL fiber's unusual flame resistance is related to the polymer structure which consists of phenolic units cross-linked with methylene units. Thus the following equation indicates that KYNOL fiber in flame converts to a carbon fiber (60 % yield)

\[
\text{KYNOL fiber} \xrightarrow{\text{flame}} \text{Carbon fiber} + \text{CO}_2 + \text{H}_2\text{O} \quad 60 \% \text{ yield}
\]

with evolution of \(\text{CO}_2\), \(\text{H}_2\text{O}\) and some \(\text{CO}\). The concentration of \(\text{CO}\) depends on both the temperature and the availability of air.

Because of its cross-linked nature, KYNOL fiber tends to convert to a glassy carbon type structure. The excellent shape retention of KYNOL fiber in a flame can be attributed to at least two factors; namely, formation of a stable cross-linked structure during charring and the relatively high carbon yield. Usually a
shrinkage in fiber length of 15% occurs during carbonization. The flame resistance of KYNOL fiber derives from several factors, which include the high carbon yield, absence of combustible gases, formation of a glassy carbon surface with minimum surface for reaction and an ablative type cooling action from the formation of H₂O and CO₂. The stability of KYNOL fiber to temperatures of even 2500°C in a torch is related to the excellent black body radiating characteristics of the carbonized surface. The efficiency of black body radiation increases by 4\textsuperscript{th} power with increasing temperature (4). There is some limitation of use of KYNOL fiber under flame conditions. For example, in atmospheres containing 40% oxygen KYNOL fiber will burn. Also extremely low density webs of KYNOL fiber at densities less than .002g/cc will flash in flame. However, the carbon fibers which are produced still retain their shape. The flash is very likely due to the fact that sufficient oxygen is available to convert immediately all the KYNOL fiber to carbon fibers. It is very important to emphasize that KYNOL fiber is not a high temperature fiber and in fact tends to degrade slowly at 200°C. Even at 150°C a slight oxidative instability has been detected in these fibers which indicates that 150°C represents the upper temperature limitation in air for long time use.

At 260°C weight loss of 40% is observed after 500 hours. Degradation reactions are undoubtedly catalyzed by oxygen since, under inert conditions, the fibers show little loss in properties even at 260°C.
5.1.2. NOMEX.

Freeston, Jr. in 1971 (11), said that NOMEX is a synthetic fiber exhibiting improved heat resistance which has replaced cotton in many special applications. However, a need still exists for a fiber with thermal characteristics superior to those of NOMEX. He found that the ignition temperature of spun NOMEX is 1600°F as compared with cotton which is 1450°F and spun PBI (Polybenzimidazole) which is 1700°F. The NOMEX fabric burning rate is .61 inch/sec and it self extinguishes after 20 seconds; (3 - 4 inches of the fabric burned).

Hendrix et al in 1972 (21) found that NOMEX maintains its high OI (Oxygen Index Value)* values over the entire temperature range studied (-50 to 250°C). This is attributable to its high thermal stability illustrated in its DTA (Differential Thermal Analysis) thermogram in Fig. 2 and TGA (Thermal Gravimetric Analysis) thermogram (22), for which thermal activity is absent until temperatures in excess of 400°C are reached. Once begun, however, the

Fig. (2) DTA thermogram for NOMEX (21)
decomposition of NOMEX is highly exothermic, and the fabric burns with a bright vigorous flame. Thus, at environmental temperatures greater than those represented by this study, NOMEX might conceivably become hazardously flammable. It must be borne in mind, however, that NOMEX retains approximately 75% residue at 500°C, a property absent in the more conventional poly-amides such as wool or nylon (22).

* OI value

The Oxygen Index, n, of a material is the minimum percentage concentration of oxygen in a mixture of oxygen and nitrogen which will maintain equilibrium burning conditions, i.e. the heat produced during combustion just balances the heat lost to the surroundings. Physically, this is the lowest concentration of oxygen which will support sustained combustion of the material, and is calculated from the following equation:

\[
    n(\%) = \frac{100 \times O_2}{O_2 + N_2} \tag{21}
\]

Where \( O_2 \) is the oxygen concentration at equilibrium and 
\( N_2 \) is the associated nitrogen concentration.
5.2. Thermal Decomposition.

Fig. 3
Combustion Apparatus.
The combustion experiments were conducted in a 3-neck flask having a capacity of 50 cc for KYNOL and 25 cc for NOMEX, which is shown in Figure (3).

The flask was weighed without the sample and with the sample before heating. After heating to 600°C for 3 minutes, using a 500 μl gas syringe*, we can take a sample while it is hot. The combustion flask was allowed to cool for 30 minutes (or more), then a reasonable amount of methanol (methanol is the best solvent for the combustion products of both KYNOL and NOMEX), was added to dissolve the condensed combustion products. By weighing the flask with the residue we can determine the weight of the residue.

*The syringe was heated to about 200°C (in an oven), so the combustion products would not be condensed on the walls of the syringe.

*The air in the flask was at atmospheric pressure.
5.3. Analysis.

Gas chromatography was the main method used in the analysis of the combustion products. As these were composed of widely differing materials, two chromatographic columns were used with a thermal conductivity detector instrument (Carle 8500).

First, a Carbosieve B (100/120 mesh) column of length 3 ft. and diameter 1/8 in., (copper column), was used with the thermal conductivity detector at 85°C column temperature and a carrier gas (helium) flow rate of 5.4 ml/min for the determination of hydrogen, nitrogen, carbon monoxide, methane, carbon dioxide, water and hydrogen cyanide.

Second, a stainless steel column, 8% GE SF 96 silicone of length 6 ft. and diameter 1/8 in., was used with the same type detector, at 85°C column temperature and a carrier gas (helium) flow rate of 7.9 ml/min, for the determination of nitrogen, water, benzene, toluene, hydrogen cyanide, methane, benzoic acid, benzamide, benzaldehyde, aniline, phenol, o-cresol, and p-cresol.
6. RESULTS


By using the carbosieve column and 200 μl sample size at the conditions mentioned in the preceding section, we got the following data for the gas standards of hydrogen, nitrogen, carbon monoxide, carbon dioxide, ammonia, hydrogen cyanide, methane and water.

Table 4.

Retention times and Response factors, By using Carbosieve column standards

<table>
<thead>
<tr>
<th>standards</th>
<th>Retention time (min.)</th>
<th>Response factors (in²/mole) × 10⁶</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen</td>
<td>.45</td>
<td>95.568</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>.69</td>
<td>101.555</td>
</tr>
<tr>
<td>Carbon monoxide</td>
<td>.80</td>
<td>103.903</td>
</tr>
<tr>
<td>Methane</td>
<td>1.80</td>
<td>9.543</td>
</tr>
<tr>
<td>Ammonia</td>
<td>3.27</td>
<td>122.551</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>3.38</td>
<td>122.648</td>
</tr>
<tr>
<td>Hydrogen cyanide</td>
<td>3.80</td>
<td>3.313</td>
</tr>
<tr>
<td>Water</td>
<td>6.03</td>
<td>75.081</td>
</tr>
</tbody>
</table>

200 μl sample size of the gas standards and 1 μl of water standard have been used.

Calculation for gas standards:

Number of moles of the gas standards from the general law of
gases, \( n \), have been calculated from the following equation:

\[
n = \frac{PV}{RT}
\]

Where

\[ P = 1 \text{ atm} \]
\[ V = 200 \mu l = 200 \times 10^{-6} \text{ liter} \]
\[ T = 294^\circ K \]
\[ R = 0.0821 \text{ liter atm/mole}^\circ K \]

\[
n = \frac{1 \times 200 \times 10^{-6}}{0.0821 \times 294} = 8.2858964 \times 10^{-6}
\]

Where the value \(8.2858964 \times 10^{-6}\) is the number of moles in 200 \( \mu l \) sample size of any gas.

Calculation for liquids:

Weight of sample = Volume \( \times \) Specific gravity

number of moles = \( \frac{\text{weight of sample}}{\text{molecular weight}} \)

Peak area:

The peaks area were determined by \( \text{Peak Height} \times \text{Middle Width} \times \text{Attenuation} = \text{in}^2 \)

Response Factor:

The response factor here means the number of square inches which corresponds to one mole of the standard (in\(^2\)/mole).
6.2. Silicone Column.

The silicone column was used at the condition mentioned before, with different sample sizes depending upon the response of each sample.

The silicone column was used for the determination of retention times, and response factors for nitrogen, carbon monoxide, water, benzene, toluene, hydrogen cyanide, methane, benzoic acid, benzamide, benzaldehyde, aniline, phenol, o-cresol and p-cresol. These data are summarized in Table (5).

Table (5). Retention Times and Response Factors by Using Silicon Column

<table>
<thead>
<tr>
<th>Standards</th>
<th>Retention Time in minutes</th>
<th>Response Factors in²/mole × 10⁻⁶</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen</td>
<td>.76</td>
<td>90.340</td>
</tr>
<tr>
<td>Carbon monoxide</td>
<td>.98</td>
<td>101.529</td>
</tr>
<tr>
<td>Water</td>
<td>1.06</td>
<td>60.310</td>
</tr>
<tr>
<td>Benzene</td>
<td>1.40</td>
<td>163.616</td>
</tr>
<tr>
<td>Toluene</td>
<td>2.43</td>
<td>223.285</td>
</tr>
<tr>
<td>Hydrogen cyanide</td>
<td>2.97</td>
<td>3.599</td>
</tr>
<tr>
<td>Methane</td>
<td>4.00</td>
<td>8.955</td>
</tr>
<tr>
<td>Benzoic acid</td>
<td>6.00</td>
<td>16.154</td>
</tr>
<tr>
<td>Benzamide</td>
<td>6.08</td>
<td>5.003</td>
</tr>
<tr>
<td>Aniline</td>
<td>7.00</td>
<td>144.279</td>
</tr>
<tr>
<td>Phenol</td>
<td>7.74</td>
<td>283.956</td>
</tr>
<tr>
<td>o-cresol</td>
<td>11.40</td>
<td>350.267</td>
</tr>
<tr>
<td>p-cresol</td>
<td>13.20</td>
<td>330.955</td>
</tr>
</tbody>
</table>
6.3. Analysis of The Combustion Products of KYNOL Fibers.

.51 g of the fibers was burned under the condition mentioned before; .14 g of the sample was vaporized.

\[
\% \text{ of residue} = \frac{(.51 - .14)}{(.51)} \times 100 = 72.55 \%
\]

The flask was heated up to 600 °C, so, the volume of the sample gases at 600 °C must be converted to the volume at the standard temperature and pressure by applying Charles and Gay-Lussac's Law as follows.

\[
\frac{V_1}{T_1} = \frac{V_2}{T_2}
\]

Where \( V_1 = 50 \text{ ml} \)

\( T_1 = 294^\circ \text{K} \)

\( T_2 = 873^\circ \text{K} \)

Then, \( V_2 = V_1 \times \frac{T_2}{T_1} \)

\( V_2 = 50 \times \frac{873}{294} = 148.47 \text{ ml} \)

The sample size was 200 μl (.2 ml), so, to calculate the weight of the combustion products inside the flask, we have to multiply by a Volume Adjusting Factor of 742.35 .

\( 148.47/2 = 742.35 \)

6.3.1. Using the Carbosieve Column.

By using the carbosieve column, the data in Table (6) were obtained for KYNOL.
Table (6). Combustion Products Analysis for KYNOL, Using The Carbosieve Column.

<table>
<thead>
<tr>
<th>R.T. (min)</th>
<th>I.D. Peaks</th>
<th>R.F. in²/mole</th>
<th>Peaks Area in²</th>
<th># of moles X10⁶</th>
<th>MW X10⁶</th>
<th>Wt X10⁶</th>
<th>VAF X10⁶</th>
</tr>
</thead>
<tbody>
<tr>
<td>.45</td>
<td>H₂</td>
<td>95.568</td>
<td>.35</td>
<td>.004</td>
<td>2</td>
<td>.007</td>
<td>5.4</td>
</tr>
<tr>
<td>.73</td>
<td>N₂</td>
<td>101.555</td>
<td>211.10</td>
<td>2.079</td>
<td>28</td>
<td>58.204</td>
<td>43207.4</td>
</tr>
<tr>
<td>.91</td>
<td>CO₂</td>
<td>103.903</td>
<td>337.92</td>
<td>3.252</td>
<td>28</td>
<td>91.064</td>
<td>67601.7</td>
</tr>
<tr>
<td>1.87</td>
<td>CH₄</td>
<td>9.543</td>
<td>16.54</td>
<td>1.733</td>
<td>16</td>
<td>27.725</td>
<td>20581.5</td>
</tr>
<tr>
<td>3.76</td>
<td>CO₂</td>
<td>122.648</td>
<td>75.30</td>
<td>.614</td>
<td>44</td>
<td>27.016</td>
<td>20055.3</td>
</tr>
<tr>
<td>6.60</td>
<td>H₂O</td>
<td>75.081</td>
<td>59.36</td>
<td>.791</td>
<td>18</td>
<td>14.231</td>
<td>10564.2</td>
</tr>
</tbody>
</table>

Where, R.T. is the Retention Time.

I.D. Peaks is the Identification of the peaks.

R.F. is the Response Factor.

MW is the molecular weight.

VAF is the Volume Adjusting Factor.

6.3.2. Using The Silicone Column.

By using the silicone column, the data in Table (7) were obtained for KYNOL.
Table (7). Combustion Products Analysis for KYNOL, Using Silicone Column.

<table>
<thead>
<tr>
<th>R.T.</th>
<th>I.D. PEAKS</th>
<th>R.F. Peaks</th>
<th># of moles</th>
<th>MW</th>
<th>Wt</th>
<th>(\chi_{VAF})</th>
</tr>
</thead>
<tbody>
<tr>
<td>min</td>
<td>in(^2)/mole</td>
<td>in(^2)</td>
<td>(\times 10^6)</td>
<td></td>
<td>(\times 10^6)</td>
<td>(\times 10^{-6})</td>
</tr>
<tr>
<td>0.75</td>
<td>N(_2)</td>
<td>90.340</td>
<td>265.66</td>
<td>2.94</td>
<td>28</td>
<td>82.32</td>
</tr>
<tr>
<td>0.95</td>
<td>CO</td>
<td>101.529</td>
<td>351.81</td>
<td>3.46</td>
<td>28</td>
<td>96.88</td>
</tr>
<tr>
<td>1.00</td>
<td>H(_2)O</td>
<td>60.310</td>
<td>71.68</td>
<td>1.19</td>
<td>18</td>
<td>21.42</td>
</tr>
<tr>
<td>1.58</td>
<td>Benzene</td>
<td>163.616</td>
<td>26.52</td>
<td>1.62</td>
<td>78</td>
<td>12.64</td>
</tr>
<tr>
<td>2.45</td>
<td>Toluene</td>
<td>223.285</td>
<td>22.37</td>
<td>1.00</td>
<td>92</td>
<td>9.20</td>
</tr>
<tr>
<td>4.10</td>
<td>Methane</td>
<td>8.955</td>
<td>9.98</td>
<td>1.12</td>
<td>16</td>
<td>18.40</td>
</tr>
<tr>
<td>7.20</td>
<td>Phenol</td>
<td>283.956</td>
<td>22.56</td>
<td>0.08</td>
<td>94</td>
<td>7.47</td>
</tr>
<tr>
<td>11.26</td>
<td>o-cresol</td>
<td>350.267</td>
<td>25.56</td>
<td>0.07</td>
<td>108</td>
<td>7.88</td>
</tr>
<tr>
<td>13.20</td>
<td>p-cresol</td>
<td>330.955</td>
<td>8.36</td>
<td>0.03</td>
<td>108</td>
<td>2.73</td>
</tr>
</tbody>
</table>

Taking the average of the two columns for carbon monoxide, methane and water, we will get the following weights.

Carbon monoxide: 0.069760

Water: 0.013232

Methane: 0.017120

From Table 6 and 7; the total weight of KYNOL combustion products is 0.1498 g
Weight of the consumed oxygen:

The volume of the oxygen in a 50 ml flask equal to 10.5 ml

Number of oxygen moles in 10.5 ml

$$n = \frac{PV}{RT}$$

$$n = \frac{1 \times 10.5 \times 10^{-3}}{.0821 \times 294} = 435 \times 10^{-3}$$

$$W = n \times M$$

Weight of consumed oxygen = 435 \times 10^{-3} \times 32 = .0139 \ g$

Weight of decomposed sample = .14 \ g $

Total weight of decomposed sample and consumed oxygen =

\[ .14 + .0139 = .1539 \]

% of the analysed materials in the total weight of decomposed materials and consumed oxygen =

\[ .1498/.1539 \times 100 = 97.33\% \]

The data in Table (8) are the percentages of the combustion products in the original sample and also in the decomposed material, in both cases the consumed oxygen has been taken in consideration.

The hydrogen gas has been detected as one of the combustion products of KYNOL, it seems to be produced from the following reaction.

$$\text{CH}_4 + \text{NH}_3 \xrightarrow{\text{heat}} \text{HCN} + 3\text{H}_2$$

Number of hydrogen moles produced (Table 6) = .004 \times 10^{-6} \ mole

Number of HCN moles produced = .004 \times 10^{-6}/3 = .003 \times 10^{-6} \ mole
Weight of HCN produced \(0.0013 \times 10^{-6} \times 27 = 0.036 \times 10^{-6}\) g

% of HCN in the decomposed material \(0.000023\)%

Table (8). % of the Combustion Products of KYNOL.

<table>
<thead>
<tr>
<th>Combustion Products</th>
<th>Weight (\times 10^6)</th>
<th>% in the original material</th>
<th>% in the decomposed material</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂</td>
<td>5.4</td>
<td>0.001</td>
<td>0.003</td>
</tr>
<tr>
<td>CO</td>
<td>69760.3</td>
<td>13.315</td>
<td>46.56</td>
</tr>
<tr>
<td>H₂O</td>
<td>13232.7</td>
<td>2.526</td>
<td>8.80</td>
</tr>
<tr>
<td>Benzene</td>
<td>9380.3</td>
<td>1.790</td>
<td>6.26</td>
</tr>
<tr>
<td>Toluene</td>
<td>6829.6</td>
<td>1.304</td>
<td>4.55</td>
</tr>
<tr>
<td>CH₄</td>
<td>17120.4</td>
<td>3.268</td>
<td>11.42</td>
</tr>
<tr>
<td>CO₂</td>
<td>20055.3</td>
<td>3.828</td>
<td>13.33</td>
</tr>
<tr>
<td>Phenol</td>
<td>5547.6</td>
<td>1.059</td>
<td>3.70</td>
</tr>
<tr>
<td>o-cresol</td>
<td>5852.7</td>
<td>1.117</td>
<td>3.90</td>
</tr>
<tr>
<td>p-cresol</td>
<td>2028.4</td>
<td>0.387</td>
<td>1.35</td>
</tr>
<tr>
<td>HCN</td>
<td>0.04</td>
<td></td>
<td>0.000023</td>
</tr>
<tr>
<td>Total</td>
<td>149813.0</td>
<td>28.5</td>
<td>97.33</td>
</tr>
</tbody>
</table>
6.3.3. Calculation of Toxicity Index.

Toxicity indices for the individual combustion products is calculated from the following equation.

\[ T = \frac{C_e}{C_f} \]

Where \( T \) is the toxicity index.

\( C_e \) is the concentration of the volatile gaseous product evolved when one gram of the original material is decomposed and the decomposition products are diffused in a volume of 1 m\(^3\) expressed in ppm.

and \( C_f \) is the concentration of gases fatal to man in 30 minutes exposure.

The total toxicity index for the combustion products of KYNOL is calculated according to the following equation.

\[ T_t = \sum \frac{C_e}{C_f} \]

Calculations of toxicity indices are summarized in Table (9). From the data in that table, the total toxicity index for KYNOL is calculated to be (1) assuming that the combined effect of toxicity is additive. Water is not considered to be toxic, but it can contribute to physiological damage by displacing oxygen.
Table (9). Toxicity indices of the combustion products of KYNOL.

<table>
<thead>
<tr>
<th>Combustion products</th>
<th>Wt produced from decomposition of one gram</th>
<th>( C^*_e ) ppm</th>
<th>( C_f ) ppm</th>
<th>T</th>
</tr>
</thead>
<tbody>
<tr>
<td>( H_2 )</td>
<td>.003</td>
<td>.40</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>CO</td>
<td>.4656</td>
<td>373.0</td>
<td>4000(20)</td>
<td>.093</td>
</tr>
<tr>
<td>( H_2O )</td>
<td>.088</td>
<td>.088</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>( CH_4 )</td>
<td>.1142</td>
<td>159.0</td>
<td>--</td>
<td>.001</td>
</tr>
<tr>
<td>( CO_2 )</td>
<td>.1333</td>
<td>68.0</td>
<td>70,000 to 100,000 (6.44)</td>
<td>.001</td>
</tr>
<tr>
<td>HCN</td>
<td>23 ( 10^{-6} )</td>
<td>.02</td>
<td>135(6)</td>
<td>.001</td>
</tr>
<tr>
<td>Benzene</td>
<td>.0626</td>
<td>.071</td>
<td>450(45)</td>
<td>.001</td>
</tr>
<tr>
<td>Toluene</td>
<td>.0455</td>
<td>.0525</td>
<td>--</td>
<td>.001</td>
</tr>
<tr>
<td>Phenol</td>
<td>.037</td>
<td>.035</td>
<td>--</td>
<td>.001</td>
</tr>
<tr>
<td>o-cresol</td>
<td>.039</td>
<td>.037</td>
<td>--</td>
<td>.001</td>
</tr>
<tr>
<td>p-cresol</td>
<td>.0135</td>
<td>.013</td>
<td>--</td>
<td>.001</td>
</tr>
</tbody>
</table>

Total toxicity index \( .101 \)

\( C^*_e \) is calculated by translating the experimental data into concentration for one gram burned, decomposed and diffused in one cubic meter of air. The weight in g is divided by density producing the volume in ml. (ml/ m\(^3\) = ppm).

A sample weight of .32 g was burned under the conditions mentioned before.

.08 g of the sample was decomposed.

% of residue = \( \frac{.32 - .08}{.32} \times 100 \) = 75 %

The flask in this case was 25 ml which is different from that used for KYNOL (50 ml).

The sample size was 200 μl (.2 ml)

\[ \frac{V_1}{T_1} = \frac{V_2}{T_2} \]

\[ \frac{25}{294} = \frac{V_2}{873} \]

\[ V_2 = 74.24 \text{ ml} \]

Volume Adjusting Factor = \( \frac{74.24}{.2} \) = 371.2

6.4.1. Using the Carbosieve Column.

By using the carbosieve column, the data in Table (10) were obtained for NOMEX.

Table (10). Combustion Products Analysis for NOMEX, Using The Carbosieve Column.

<table>
<thead>
<tr>
<th>R.T.</th>
<th>I.D.</th>
<th>R.E.</th>
<th>Peaks</th>
<th># of moles</th>
<th>M W</th>
<th>Wt.</th>
<th>XAVF</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>min.</td>
<td>Peaks in²/mole</td>
<td>Area in²</td>
<td>X10⁶</td>
<td></td>
<td>g</td>
<td></td>
</tr>
<tr>
<td>.71</td>
<td>N₂</td>
<td>101.555</td>
<td>80.90</td>
<td>1.77</td>
<td>28</td>
<td>49.56</td>
<td>.018397</td>
</tr>
<tr>
<td>.89</td>
<td>CO</td>
<td>103.903</td>
<td>229.82</td>
<td>2.21</td>
<td>28</td>
<td>61.88</td>
<td>.022970</td>
</tr>
<tr>
<td>1.88</td>
<td>CH₄</td>
<td>9.543</td>
<td>1.10</td>
<td>.12</td>
<td>16</td>
<td>1.92</td>
<td>.000713</td>
</tr>
<tr>
<td>3.4</td>
<td>CO₂</td>
<td>122.648</td>
<td>289.84</td>
<td>2.36</td>
<td>44</td>
<td>103.84</td>
<td>.038545</td>
</tr>
<tr>
<td>3.6</td>
<td>HCN</td>
<td>3.313</td>
<td>2.48</td>
<td>.75</td>
<td>27</td>
<td>20.25</td>
<td>.007517</td>
</tr>
<tr>
<td>6.4</td>
<td>H₂O</td>
<td>75.081</td>
<td>35.06</td>
<td>.52</td>
<td>18</td>
<td>9.36</td>
<td>.003474</td>
</tr>
</tbody>
</table>
6.4.2. Using The Silicone Column.

By using the silicone column, the data in Table (11) were obtained for NOMEX.

Table (11). Combustion Products Analysis For NOMEX, Using The Silicone Column.

<table>
<thead>
<tr>
<th>R.T. min.</th>
<th>I.D. Peaks</th>
<th>R.P. in /mole</th>
<th>Peaks in²</th>
<th># of moles X10⁶</th>
<th>M.W</th>
<th>Wt. g</th>
<th>VAF g</th>
</tr>
</thead>
<tbody>
<tr>
<td>.71</td>
<td>N₂</td>
<td>90.340</td>
<td>165.86</td>
<td>1.84</td>
<td>28</td>
<td>51.52</td>
<td>.019124</td>
</tr>
<tr>
<td>.90</td>
<td>CO</td>
<td>101.529</td>
<td>220.22</td>
<td>2.17</td>
<td>28</td>
<td>60.76</td>
<td>.022554</td>
</tr>
<tr>
<td>1.30</td>
<td>H₂O</td>
<td>60.310</td>
<td>6.48</td>
<td>.11</td>
<td>18</td>
<td>1.98</td>
<td>.000735</td>
</tr>
<tr>
<td>1.50</td>
<td>Benzene</td>
<td>163.616</td>
<td>13.60</td>
<td>.08</td>
<td>78</td>
<td>6.24</td>
<td>.002316</td>
</tr>
<tr>
<td>2.23</td>
<td>HCN</td>
<td>3.599</td>
<td>2.48</td>
<td>.69</td>
<td>27</td>
<td>18.63</td>
<td>.006916</td>
</tr>
<tr>
<td>6.75</td>
<td>Aniline</td>
<td>144.279</td>
<td>2.26</td>
<td>.02</td>
<td>93</td>
<td>1.86</td>
<td>.000690</td>
</tr>
</tbody>
</table>

Taking the average of CO, H₂O, and HCN in the two columns.

Average wt of CO = .0228 g
Average wt of H₂O = .0021 g
Average wt of HCN = .0072 g

Weight of consumed oxygen, will be added to the decomposed weight of the sample.

The volume of the flask is 25 ml, 21% of this volume is oxygen. i.e. the volume of oxygen = 25 x 21/100 = 5.25 ml.
Number of moles of consumed oxygen \( (n) \)  \( \frac{PV}{RT} \)

\[
n = \frac{1}{0.0821 \times 294} \times 5.25 \times 10^{-3} = 0.21751 \times 10^{-3} \text{ mole}
\]

Weight of oxygen \( (W) \)

\[
W = n M = 0.21751 \times 10^{-3} \times 32 = 6.96 \times 10^{-3} \text{ g}
\]

\[= 0.00696 \text{ g} \]

Weight of the analysed combustion products = 0.074347 g

Weight of decomposed material and consumed oxygen = 0.08 + 0.00696 = 0.08696 g

\% of the analysed material in the decomposed material

\[
\frac{0.074347}{0.08696} \times 100 = 85.5 \%
\]

The following data in Table (12) are the percentages of the combustion products in the original material and the decomposed material.

<table>
<thead>
<tr>
<th>Combustion Products</th>
<th>Weight g</th>
<th>% in the original material</th>
<th>% in the decomposed material</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>0.022762</td>
<td>6.96</td>
<td>26.18</td>
</tr>
<tr>
<td>H₂O</td>
<td>0.002105</td>
<td>0.64</td>
<td>2.42</td>
</tr>
<tr>
<td>HCN</td>
<td>0.007216</td>
<td>2.20</td>
<td>8.30</td>
</tr>
<tr>
<td>CH₄</td>
<td>0.000713</td>
<td>0.22</td>
<td>0.82</td>
</tr>
<tr>
<td>CO₂</td>
<td>0.038545</td>
<td>11.79</td>
<td>44.33</td>
</tr>
<tr>
<td>Benzene</td>
<td>0.002316</td>
<td>0.71</td>
<td>2.66</td>
</tr>
<tr>
<td>Aniline</td>
<td>0.000690</td>
<td>0.21</td>
<td>0.79</td>
</tr>
</tbody>
</table>
6.4.3. Calculation of Toxicity Index.

Toxicity indices for the individual combustion products of NOMEX, and its total toxicity index were calculated as mentioned before in 6.3.3. The toxicity data are summarized in table (13).

Table (13). Toxicity indices of the combustion products of NOMEX.

<table>
<thead>
<tr>
<th>Combustion Products</th>
<th>Wt produced from decomposition of one gram</th>
<th>C_e ppm</th>
<th>C_f ppm</th>
<th>T</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>.2618</td>
<td>209.00</td>
<td>4000(20)</td>
<td>.052</td>
</tr>
<tr>
<td>H_2O</td>
<td>.0242</td>
<td>.02</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>HCN</td>
<td>.0830</td>
<td>88.00</td>
<td>135(6)</td>
<td>.653</td>
</tr>
<tr>
<td>CH_4</td>
<td>.0082</td>
<td>11.00</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>CO_2</td>
<td>.4433</td>
<td>224.00</td>
<td>70,000 to 100,000 (6,44)</td>
<td>.003</td>
</tr>
<tr>
<td>Benzene</td>
<td>.0266</td>
<td>.03</td>
<td>450(45)</td>
<td>.001</td>
</tr>
<tr>
<td>Aniline</td>
<td>.0079</td>
<td>.008</td>
<td>--</td>
<td>.001</td>
</tr>
</tbody>
</table>

Total toxicity index .710

C_e is calculated as mentioned before in Table (9).

The total toxicity index of the combustion products of NOMEX is calculated to be .71, assuming that the combined effect of toxicity is additive. Water is not considered to be toxic, but it can contribute to physiological damage by displacing oxygen.
7. DISCUSSION


Both fibers were heated up to 600°C under the same conditions. From the analysis of the combustion products, we can see that the percentage of CH\textsubscript{4} produced from decomposed KYNOL sample is 11.42% (Table 8), while the percentage produced from NOMEX sample is much lower (0.82%, Table 12). This is due to the absence of alkyl groups in the chain of NOMEX fibers.

From Table 8 and 12, we can see that the summation of CO and CO\textsubscript{2} percentages are 59.89% in KYNOL and 70.51% in NOMEX and this is due to the presence of carbonyl groups in the chain of NOMEX fibers.

The percentage of H\textsubscript{2}O in KYNOL is 8.8% and that from NOMEX is
2.42 %. This is due to the presence of hydroxyl groups, and also methylene groups in the chain of KYNOL fibers.

HCN produced in case of KYNOL is due to the fact that the fibers have been treated with ammonia. This trace of ammonia may react with the methane produced from the combustion to form 3 moles of hydrogen and one mole of HCN (the equation is on page 46). The hydrogen was readily detected (right before the nitrogen peak using the carbosieve column) due to its high response factor, which is 30 times as that of HCN. HCN is calculated as 1/3 of the number of hydrogen moles produced.

The HCN produced from NOMEX (8.3 % from the decomposed material) is due to the distortion of the phenyl group carrying NH groups in the chain of NOMEX.

Benzene was produced with a percentage of 6.26 % in case of KYNOL, which is higher than that produced from NOMEX (2.66 %) due to the presence of cross linkage in KYNOL fibers, which makes it more difficult to decompose.

Phenol, o-cresol and p-cresol, were detected in the combustion products of KYNOL, Thus, not only verifying the structure of KYNOL, but also indicating that the fiber has a strong cross linkage. Because the percentage of p-cresol is 1.35 % as compared to that of o-cresol which is 3.9 %, we can say that, the strength of the cross linkage is approximately 3 times stronger than the chain bond. The ortho position (chain bond) is more crowded than the para position.
(cross linkage bond), so it will be easier to break the ortho position than the para position.

The production of phenol with approximately the same percentage as o-cresol, verifies this explanation, that the probability of breaking the methylene group on both sides is the same.

The production of aniline in the combustion products of NOMEX, verify the structure. Also its low percentage (0.79 %) indicates that the tendency for distortion of the phenyl group to produce low molecular weight products is more than just to crack the monomer to produce aniline.

Benzaldehyde, was suggested as a possible combustion product of NOMEX, but it could not be detected. This may be due to, its low amount, its low response or the tendency of the carbonyl groups to form CO and CO₂ gases more readily than benzaldehyde due to the deficiency of hydrogen in the molecule.

The high percentage of residue of KYNOL (72.55 %) verifies the fact that KYNOL has unusual flame resistance due to its polymer structure (9) which consists of phenolic units cross linked with a methylene units.

Percentage of residue in case of NOMEX was 75%, verifying the fact that NOMEX has an excellent thermal stability. This was proved before by Hendrix et al (21), by determining the NOMEX oxygen index value (OI). It is very high, which demonstrates its high thermal stability.
The percentage of the detected combustion products in the decomposed material of KYNOL was 97.33 %, and in case of NOMEX was 85.5 %. The rest is unidentified materials, which has been detected, some other unidentified materials, and also, some monomers, dimers and low polymers. While we have identified and quantified the bulk of the combustion products, further investigations could be done on these materials.
7.2. Combustion Products and Toxicity.

The main toxic products produced were CO and HCN in both fibers, also CO$_2$ and benzene which have been taken in consideration. Other products such as aniline, phenol, o-cresol, p-cresol and toluene, could not be considered because their C$_f$ values are not known. These compounds, however, are present in low concentration and their contribution to the toxicity may well be neglected.

The toxic effect was assumed to be additive. This assumption may be conservative because of possible synergistic effects. Synergism may have to be considered in the future for certain combinations of toxic products, if it is found to be significant.

The toxicity due to HCN was found to be 30 times as great as that due to CO. The toxicity due to HCN produced from KYNOL, due to the trace of ammonia present in the sample; thus, the amount of HCN produced depend upon the amount of ammonia in the sample. The toxicity due to HCN produced from NOMEX was found to be 12 times as great as that due to the other products.

The total toxicity of the combustion products of decomposition of one gram of KYNOL was found to be .1 and that of NOMEX was found to be .7. This can be interpreted to mean that, if one gram of KYNOL was decomposed and the combustion products were diffused in one cubic meter of air, the probability of dying for a man in that space after 30 minutes exposure is 10 %, and that of NOMEX is 71 %.

The total toxicity index of KYNOL and NOMEX is compared with other polymers in table (14).
<table>
<thead>
<tr>
<th>Polymer</th>
<th>Toxicity Index</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acrylic Fiber</td>
<td>1.21</td>
<td>44</td>
</tr>
<tr>
<td>NOMEX</td>
<td>.71</td>
<td></td>
</tr>
<tr>
<td>Nylon</td>
<td>.52</td>
<td>44</td>
</tr>
<tr>
<td>Wool</td>
<td>.38</td>
<td>44</td>
</tr>
<tr>
<td>PVC</td>
<td>.36</td>
<td>45</td>
</tr>
<tr>
<td>Urea-formaldehyde foam</td>
<td>.27</td>
<td>44</td>
</tr>
<tr>
<td>Rigid urethane foam</td>
<td>.10</td>
<td>44</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>.10</td>
<td>44</td>
</tr>
<tr>
<td>KYNOL</td>
<td>.10</td>
<td></td>
</tr>
<tr>
<td>White pine</td>
<td>.09</td>
<td>44</td>
</tr>
</tbody>
</table>
8. CONCLUSIONS

The quantitative analysis of the combustion products produced from KYNOL and NOMEX could explain the polymer structure, at the same time it could explain the properties of the polymer.

HCN was produced from both fibers which is 30 times as toxic as CO. In case of KYNOL fibers, HCN may be produced from the reaction of ammonia with methane, so, the ammonia in KYNOL fibers should be removed completely to avoid the production of HCN.

The toxicity of the combustion products of NOMEX is higher than the average (Table 14) of the other polymers; so, the use of large quantities of its fabrics in any place, where, there is a probability of fire is not recommended, inspite of its self extinguishing properties.
9. REFERENCES


