

UNIVERSITY OF CALGARY

FACTORS INFLUENCING THE CHLORINATION AND STABILITY
OF UREA-MELAMINE-FORMALDEHYDE RESINS

by

SOHAIR I. ABO EL-EIA

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES
IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE
OF MASTER OF SCIENCE

DEPARTMENT OF CHEMISTRY

CALGARY, ALBERTA

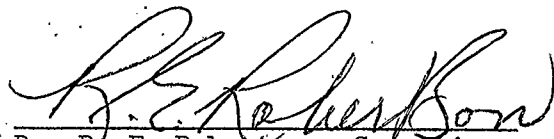
SEPTEMBER, 1972

© S. I. Abo El-Eia, 1972

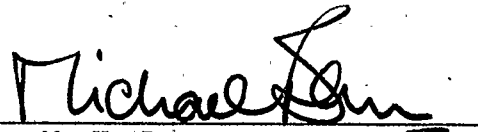
THE UNIVERSITY OF CALGARY

FACULTY OF GRADUATE STUDIES

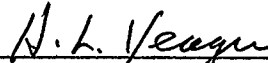
The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies for acceptance, a thesis entitled "Factors Influencing the Chlorination and Stability of Urea-Melamine-Formaldehyde Resins" submitted by Sohair I. Abo El-Ela in partial fulfillment of the requirements for the degree of Master of Science.



Dr. R. E. Robertson, Supervisor
Department of Chemistry



Dr. M. H. Benn
Department of Chemistry



Dr. H. L. Yeager
Department of Chemistry



Dr. G. A. Gregory
Department of Chemical
Engineering

DATE: September 28, 1972

ABSTRACT

Factors influencing the chlorination of urea-melamine-formaldehyde resin for eight different formulations have been studied. The effect of pH, chlorine concentration, grain size, resin amount, temperature, added chlorite, chlorate, and chloride to the chlorinating medium were investigated. The stability of such chlorinated resins chlorinated under the above conditions was studied. The rates of oxidation of UMF resins during chlorination and in static water were determined. In addition, a hypothesis for the mechanism of self-oxidation of these resins during the chlorination process is proposed.

ACKNOWLEDGEMENTS

I would like to express my deep sense of gratitude to Dr. R. E. Robertson whose constant encouragement and guidance helped me to start, continue and finish this thesis.

Thanks are due to the National Research Council of Canada, and the University of Calgary for providing financial assistance to this work.

The author would also like to thank Dr. D. P. Horning for his valuable discussions, Mr. R. Wilton, Mr. D. Malinski for their technical help. Thanks are also extended to Miss S. Cranch for the typing of this manuscript.

WITH MY LOVE

TO

GAMAL AND DALIA

TABLE OF CONTENTS

	PAGE
LIST OF TABLES	iii
LIST OF FIGURES	v
CHAPTER ONE	
INTRODUCTION	1
1.1 N-Chloro Compounds	2
1.1.1 Chlorine exchange resins	3
1.1.2 Urea-melamine-formaldehyde resin	5
1.1.3 Relation between N-chloro compounds and chlorine exchange resins.	7
1.2 Principles of Chlorine Exchange	8
1.3 Stability of N-Chloro Compounds	11
1.4 Objective of Thesis..	12
CHAPTER TWO	
FACTORS INFLUENCING CHLORINATION	13
2.1 Introduction	13
2.2 A general Account of the Probable Structure of UMF Resin	16
2.3 A typical Run of the Chlorination Process	18
2.4 Experimental Results	19
2.4.1 Series 1	20
(a) Effect of pH	20
(b) Effect of chlorine concentration	23
(c) Effect of grain sizes	24
(d) Effect of added chlorite, chlorate and chloride ions on chlorination	27
2.4.2 Series 2 and 3	32
2.4.3 Series 4	33
2.5 Rate of Oxidation of Chlorinated UMF Resins	35

	PAGE
2.6 Conclusion	42
CHAPTER THREE	
STABILITY OF CHLORINATED UMF RESINS	44
3.1 Introduction	44
3.2 Measurements of Self-Oxidation of Chlorinated UMF Resins Under Various Conditions	45
3.3 Multiple Chlorination Process	53
3.4 Gas Analysis	58
3.5 A Hypothesis for the Mechanism of Self-oxidation of Chlorinated UMF Resins	60
3.6 Conclusion	73
CHAPTER FOUR	
EXPERIMENTAL	74
4.1 Preparation of Materials	74
4.1.1 Purity of water	74
4.1.2 Preparation of sodium hypochlorite solution . . .	74
4.2 Description of Apparatus	75
4.2.1 Apparatus for chlorinating and measuring the self- oxidation of the resin	75
4.2.2 Apparatus for self-oxidation test	80
4.3 Analyses	81
4.3.1 Analysis of positive chlorine	81
4.3.2 Gas analysis	82
CHAPTER FIVE	
CONCLUSION	84
REFERENCES	87

LIST OF TABLES

<u>Table No.</u>	<u>Title</u>	<u>Page No.</u>
2.1	Percent of total available chlorine present in the form of HOCl.	14
2.2	Percent of total chlorine in hypochlorite solutions present as hypochlorous acid at various pH levels, 25°C.	15
2.3	Different formulations for chlorine exchange resin.	17
2.4	Effect of pH on chlorination of resin 53-1 at 10°C.	20
2.5	Effect of active chlorine concentration on resin 53-1, chlorinated at pH 4 and 10°C.	23
2.6	Variation of chlorine capacity of the resin with time, chlorinated at pH 4, 10°C and initial Cl* = 0.160 M.	24
2.7	Effect of grain size of resin 53-1 on the total amount of NaOH and the wt % of the combined chlorine in the resin, chlorinated at pH 5 and 10°C.	25
2.8	Effect of the amount of resin on the wt % chlorine and the total amount of NaOH, at pH 5 and 10°C.	27
2.9	Effect of added chlorite on chlorination of resin 53-1 chlorinated at pH 5 and 10°C.	28
2.10	Effect of temperature on chlorination at pH 4 and 5, grain size 20-40 mesh and initial Cl ₂ = 0.122 M.	32
2.11	Effect of polymer composition on chlorination at pH 4, 20°C.	34
2.12	Data for determining the rate of oxidation of resin 53-1 at pH 5 and 10°C.	37
2.13	Data for determining the rate of oxidation of resin 53-1 at pH 4 and 40°C.	38
2.14	Effect of different temperatures on the rate of oxidation for resin 53-1 at pH 5.	41

<u>Table No.</u>	<u>Title</u>	<u>Page No.</u>
2.15	Effect of different compositions of UMF resin on the rate of oxidation, chlorinated at 20°C and pH 4.	42
3.1	Comparison of the gases released from 1 g samples of resin 53-1 and 144-1 chlorinated at pH 4 and 20°C.	46
3.2	Comparison of the gas evolution from resin 53-1 and 144 series chlorinated at pH 4 and 20°C.	48
3.3	Effect of different temperature of chlorination on the stability of the resin 53-1 at pH 5.	51
3.4	Wt % of chlorine in the prechlorinated resins at 20°C and pH 4.	54
3.5	Comparison of the gases released from the resins chlorinated according to both ordinary and multiple chlorination	58
3.6	% of relative intensity of the gases evolved from resin 53-1 chlorinated at pH 6 and 10°C.	59
3.7	% of the gases evolved from resin 144-3 chlorinated at pH 4 and 20°C.	60
3.8	Effect of light on the evolution of gases from resin 53-1 chlorinated at 20°C and pH 5.	63
3.9	Effect of added antioxidant to resin 53-1 chlorinated at pH 5 and 20°C.	64

LIST OF FIGURES

<u>Figure No.</u>	<u>Title</u>	<u>Page No.</u>
2.1	Rate of oxidation of resin 53-1 at pH 5 and 10°C.	39
2.2	Rate of oxidation of resin 53-1 at pH 4 and 40°C.	40
3.1	The amount of gases released from resins 53-1 and 144-1 chlorinated at pH 4 and 20°C.	47
3.2	The amount of gases released from resins 53-1, 144-1, 144-2, 144-3 and 144-4 chlorinated at pH 4 and 20°C.	49
3.3	The amount of gases released from resins 144-5, 144-6, 144-7 and 144-8 chlorinated at pH 4 and 20°C.	50
3.4	The amount of gases released from resin 53-1 chlorinated at different temperatures.	52
3.5	The amount of gases released from resin 53-1 chlorinated according to both ordinary and multiple chlorination processes at pH 4 and 20°C.	56
3.6	The amount of gases released from resin 144-2 chlorinated according to both ordinary and multiple chlorination processes at pH 4 and 20°C.	57
4.1	Block diagram for the system used for the chlorination process.	77
4.2	Comparator output.	79

Chapter One

INTRODUCTION

The treatment of water with chlorine as a means of killing germs has a long history and is widely used^{1,2,3,4,5,6,7}. The utility of chlorine in water treatment is attributable to its toxicological characteristics^{8,9,10,11,12,13} and its oxidative capacity^{7,11,14,15}. The amounts required for these purposes are usually small, a fortunate requirement since chlorine is both an irritant and, at somewhat higher concentrations, is toxic.

Since natural water may have some oxygen-demand which will have to be met by any added chlorine, a satisfactory method of introducing chlorine into a water system at the required low concentration for bacteriocidal purposes (< 1.ppm) must also provide for some means of satisfying this variable oxygen-demand. Maintenance of chlorine concentration in water supplies at the required low level, while relatively simple for large treatment centres with the necessary metering and analytical systems, is far less convenient for the small user.

For this reason the announcement of Wayman¹⁶ of the invention* of a chlorinated polyamide resin which could be described to act both as a "chemical-valve" and a "store", was regarded as having wide application. It was claimed that¹⁶ this chlorinated polyamide resin would introduce the requisite amount of chlorine into a water system

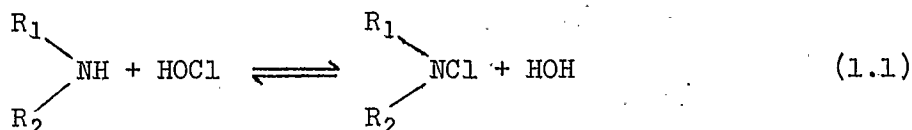
* There is a patent on the production and use of N-chlorinated resins as "exchange resins" for positive chlorine written by Goodman, Solomon, U.S. pat. 2,944,033(1960) which made the invention of Wayman less novel.

to satisfy variable oxygen demand and leave a residual of chlorine sufficient for bacteriocidal purposes ... cheaply and easily.

This property attributed to the chlorinated polyamides is an example of the general character of N-chloro compounds to establish a low equilibrium concentration of active chlorine in water.

1.1 N-chloro Compounds:

The N-chlorination of amides, amines, imine, imides and aminoazines can be represented by the equation:



These reactions have been studied by Soper et al^{17,18,19,20,21,22} and more recently by Wayman and Thomm^{23,24,25}.

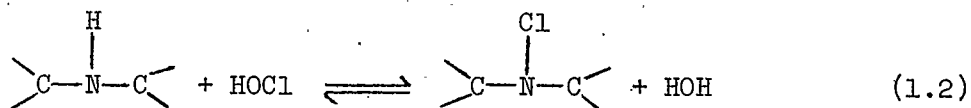
The term usually used²⁶ for all of the N-chloro compounds is "chloramine" (or "chloroamine") which includes all compounds containing one or more chlorine atoms attached to nitrogen, e.g. chloramines, chlorimines, chloramides, and chloroimides. The reaction (1.1) from right to left is a hydrolysis where the hydrolysis constant depends on the (R) groups. For most amides and amines, the hydrolysis constants are small²⁷ (10^{-4} to 10^{-8}) and allow a small but appreciable amount of hypochlorous acid liberation to an aqueous medium. This limited hydrolysis is the unique chemical characteristic which enables the use of N-chloro compounds such as chloramine T^{28,29}, chloroisocyanuric acid^{30,31}, N-chlorosuccinimide^{21,22}, and trichloromelamine³² as chlorinating agents in water and the use of

the unchlorinated forms of these compounds such as cyanuric and sulfamic acids to stabilize the chlorination of water.

These N-chloro compounds are more popular than chlorine solutions (e.g. Javex) because their positive chlorine is often more stable than chlorine solutions and easier to handle.

1.1.1 Chlorine exchange resins:

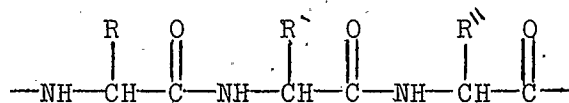
Chlorine exchange resins¹⁶ are polymeric materials containing nitrogen groups (amide, imide, amine and triamino-triazine) that are capable of undergoing the following substitution reaction:



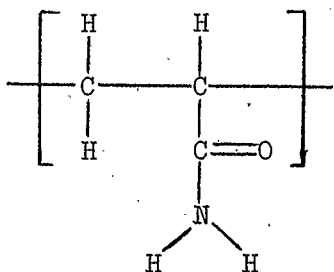
By analogy with other N-chloro compounds, polymers containing -NH and/or -NH₂ groups should be applicable for use as chlorine exchange under some, if not all, conditions. The potential advantage of such chlorinated polyamide resins is that the "back bone" is not released to the water system in the reversal of equation (1.2).

The preferred physical form of such resins would be beads similar to the better known ion exchange resins. The particles should have reasonable dimensional stability and be insoluble in the chlorination medium and water, but nevertheless be hydrophilic enough to absorb water and allow accessibility to the nitrogen groups. The resins must be crosslinked enough to hold them together but still allow for swelling and/or water absorption³³. Polymers that fulfill the above requirements are proteins, polyacrylamides, polyamides, polyurethanes, and amino-resins.

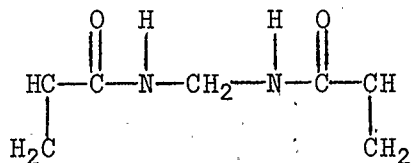
In principle, proteins are well suited to be chlorine exchange resins. The structure is characterized by the formula



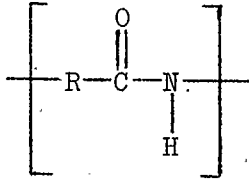
where R, R' and R'' are the residues of the amino acids and are generally different. Proteins can be crosslinked, using urea, to make them insoluble in water. The polyacrylamides are water soluble polymers with the general formula:



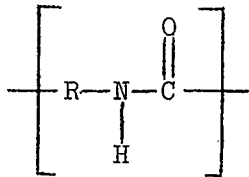
These polymers can also be made insoluble in water by crosslinking. For example, Methylene bisacrylamide



undergoes vinyl polymerization, either alone or as a co-polymer with acrylamide, to produce an insoluble crosslinked polymer. Polyamides such as nylon provide another type of potential chlorine exchange resins. The basic structure of these polyamides is as follows:



Likewise, polyurethanes can be used as chlorine exchange resins. The general structure is:



The monomeric materials here are di and tri-isocyanates.

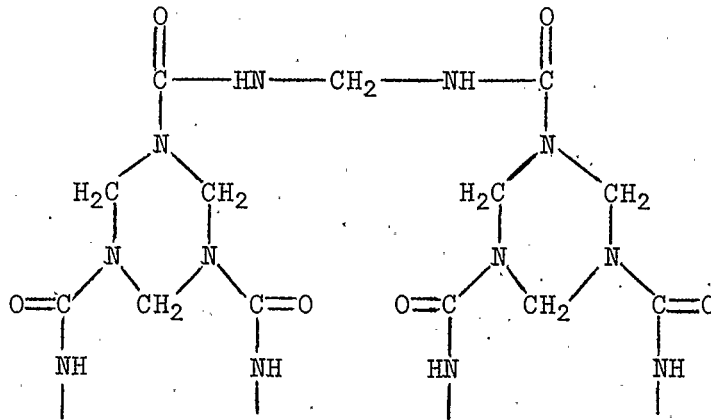
In practice none of the above N-chloro resins have provided a useful means for water treatment. In contrast, the urea-melamine-formaldehyde resin gave promise of providing a practical means for treating water with chlorine.

1.1.2 Urea-melamine-formaldehyde resins:

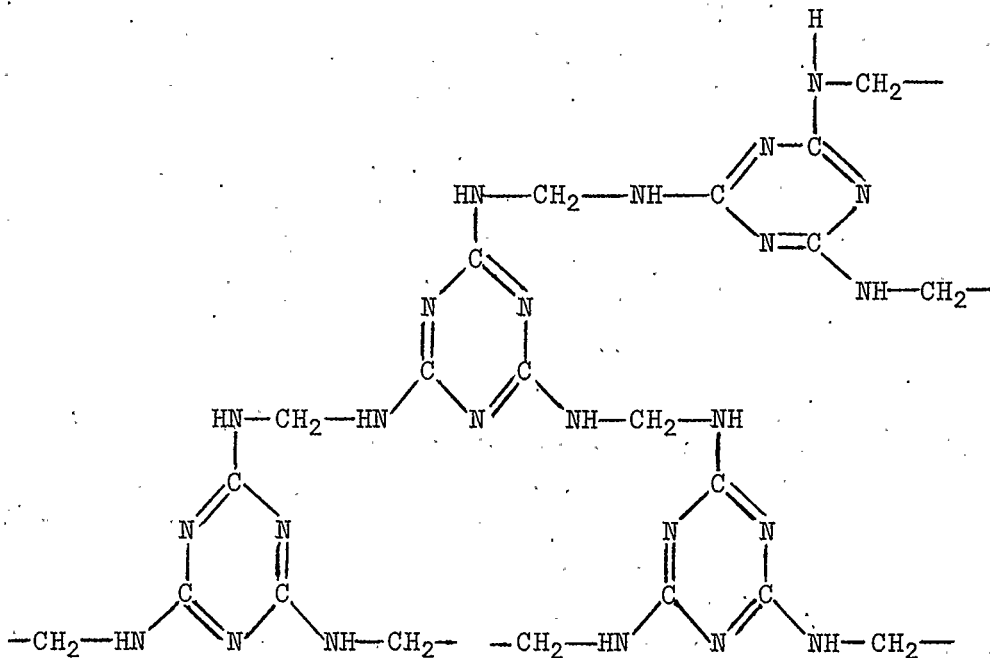
Urea-melamine-formaldehyde resins (UMF resins) have a long history^{34,35} and have found wide application in such familiar forms as Melamine dishes, decorative laminates, ion exchange resins, and adhesives. These forms are generally highly crosslinked and impervious to water. However, by suitable adjustment of proportions and conditions, a "macro reticular"¹⁶ form can be synthesized. These forms were exploited by Wayman and co-workers^{16,23,24,25}. The latter resins are the most interesting polymers from a chlorine exchange point of view, since they are easily produced from cheap, easily available chemicals. The work reported in this thesis is mainly

concerned with this type of resin.

Urea-formaldehyde resins are formed by condensing urea with formaldehyde using 1 to 2 fold excess of formaldehyde. Several mechanisms have been suggested^{36,37} and it seem likely that the final structure of urea-formaldehyde can be represented as follows:



In a similar manner melamine-formaldehyde resins may be represented by the formula³⁹



The possibility that any of these UMF resins will find application depends in varying degrees on such factors as cost, structure, the value of the equilibrium constant, and stability.

1.1.3 Relation between N-chloro-compounds and chlorine exchange resins:

Chlorine exchange resins undergo the same chemical process as the monomeric N-chloro compounds. That is, they react with chlorine in a chlorine-rich aqueous medium (left to right, equation (1.2)) and liberate this chlorine, via hydrolysis, when exposed to an aqueous medium in which chlorine is absent or present in a concentration that is lower than the equilibrium value (as a consequence of a chlorine demand). But there are significant differences. The chlorinated polyamides are set apart from numerous other chlorinated-amides used in commerce as a "solid form of chlorine" because of the insolubility of the polymer: the >NH group forming part of an insoluble chain. The residual $\begin{array}{c} \text{H} \\ | \\ \text{C}-\text{N}-\text{C} \\ / \quad \backslash \end{array}$ on the left-hand side of the equilibrium (equation (1.2)) is part of cross-linked insoluble polymer and hence is not added to the water supply.

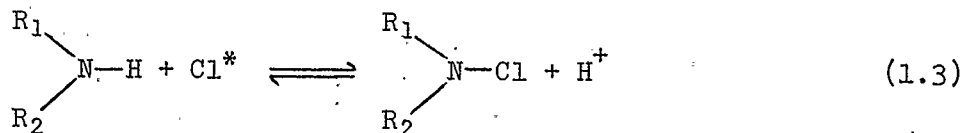
Also, if we consider the chlorine exchange resins to behave in a fashion similar to the monomeric chloramine, there may be a second factor to be considered: the rate of absorption and liberation of available chlorine may be altered by diffusion control rather than reaction control alone³³.

Thus, the phenomenon involved in the transfer of chlorine to and from the particles of insoluble cross-linked polymers creates a new approach to the chlorination of an aqueous medium which will

be discussed in greater detail in the following section.

1.2 Principles of Chlorine Exchange:

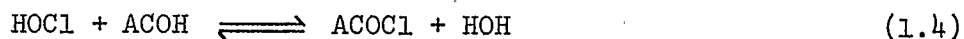
The process of chlorine exchange may be represented in a general form by the equation:



where the chlorine maintains its valence state of +1 in both compounds.

It is important to recognize that the Cl^* probably has no separate existence but occurs in combination with a "carrier" e.g. OCl^- , $HOCl$,

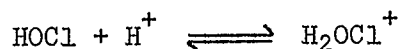
$CH_3-\overset{O}{\parallel}-OCl$, $R-\overset{O}{\parallel}-OCl$, etc. The OCl^- ion is probably an active species at high pH. At low pH (<5) and in the presence of acetate ions, Soper and co-workers^{17,18,19,20} have shown that acetyl hypochlorite is formed and it reacts more readily with nitrogen.



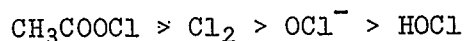
By analogy other acid ions would be expected to act similarly. It was proposed by de la Mare and his co-workers^{39,40} that the electro-positive chlorinium ion, Cl^+ , was a possible chlorinating agent in analogy with the "nitronium ion". It was proved by Swain⁴¹ that it is extremely improbable that the chlorinium ion, Cl^+ , is significantly involved in the chlorination process. No term in the rate law is

* Cl^* or "active" chlorine or "positive" chlorine: the term "positive chlorine" or Cl^* or active chlorine refers to that chlorine in N-chloro compounds and hypochlorous acid which may be considered to have a valence of +1.

consistent with rate-determining formation of the chlorinium ion. Although the Cl^+ mechanism has been publicized in many excellent textbooks, however, the thermodynamic arguments show that Cl^+ is highly unstable relative to coordinated species. For dissociation of Cl_2 to Cl^+ and Cl^- in water at 25°C , the estimated equilibrium constant is 10^{-40} , from which it can be calculated that $[\text{Cl}^+]$ is less than 10^{-40}M under conditions where the zero-order dependence on organic substrate was observed. Swain showed that the kinetic terms in chlorination are directly analogous with the corresponding conversions of HO-Cl to the more reactive chlorinating agents, ClO-Cl , Cl-Cl , and, possibly, H_2OCl^+ . However, a further possibility of the chlorinating agents is the formation of the protonated hypochlorous acid species,⁴²



Such ions are powerful electrophilic agents and would be expected to react with the nucleophilic nitrogen. Wayman and Thomm²⁴ found that the absence of dependence of the HOCl reaction rates on pH argues against this formulation. They proposed that in the absence of additives, and in the pH region of undissociated hypochlorous acid, the active N-chlorinating species is the acid itself, i.e., HOCl . The relative reactivity of the chlorinating reagents with secondary amides was found to have the sequence



Let us now consider the principle of using N-chloro compounds as a source of active chlorine. When N-chloro compounds such as

chloramine T, trichloromelamine, N-chlorosuccinimide are in water they liberate "active chlorine" until the corresponding equilibrium concentration is reached. Where a substance is present in water which creates an "oxygen-demand", the active chlorine thus released reacts (bleaching, disinfecting, etc.) and further chlorine (combined available chlorine)* will be liberated from the N-chloro compounds to maintain equilibrium (equation 1.1). By the proper choice of carrier²⁶, various equilibrium concentrations of "free available chlorine"*** may be maintained at the value required for disinfecting or bleaching.

The UMF resins, which are considered to contain similar structures (Section 1.1.2) were found to maintain equilibrium concentration in the same range as these monomolecular analogues. Specifically, Wayman and Dewar found this value to be 2-3 ppm. This may be somewhat higher than the long term equilibrium concentration⁴⁵.

In terms of practical application, it will be noted that

* "Available chlorine": The available chlorine content of a compound is expressed in terms of the amount of elemental chlorine that would have the same oxidizing power. The "available" chlorine group of compounds are those when dissolved in or in contact with water liberate hypochlorous acid or (OCl⁻).

"Free" available Chlorine: refers to chlorine present as hypochlorous acid or hypochlorites or dissolved elemental chlorine.

** "Combined" available chlorine: refers to chlorine present as N-chloro compounds which usually have less reactivity than hypochlorites.

the N-chloro compounds do not themselves take part in the disinfecting or bleaching process; it is the HOCl, ClO⁻ or Cl₂ which act as the active agents. The chlorine atom in hypochlorous acid and N-chloro compounds have a valence of +1 (Cl⁺) and when acting as an oxidizing agent this positive chlorine undergoes a valence change of two (+1 to -1), whereas the chlorine atoms in Cl₂ undergo an average valence change of one (0 to -1). Therefore, one atom of Cl* is equivalent in oxidizing power to one molecule of Cl₂.

Clearly, the equilibrium concentration of active chlorine is one of the factors important to the production of chlorine-exchange resin suitable for application in the treatment of potable water. But beyond a certain minimum level of chlorine, the stability of the resin to resist self-oxidation becomes an even more critical factor.

1.3 Stability of N-chloro compounds:

The question of "stability" in connection with the application of such chloro-compounds to water treatment covers many considerations:

1. At a higher concentration of HOCl, many oxidation reduction reactions are to be expected (Chapter 2). However, at the concentration of active chlorine available in this study, it is doubtful if these reactions are significant.
2. In general, the stability of Cl* is directly related to the number of chlorine atoms on the nitrogen. N-chlorinated secondary amide nitrogen is more stable than primary⁴³, while trichloroamine is

very unstable.

3. Decomposition is found to be greater in solution than in the dry solid form⁴⁴.
4. Temperature and pH value can be considered also as factors which affect stability. At higher temperature, N-chloro compounds were found to be more unstable than at lower temperature. Variations in pH seems less important. It will be apparent that the above factors have practical implications which require consideration in the production of a practical chlorine exchange resin for treatment of water.

1.4 Objective of Thesis:

The objective of the study reported here comes directly from the fact that the chlorine-exchange resin produced by Wayman and Dewar^{16,34} and protected by Canadian Patent No. 849614 proved so unstable as to be unserviceable in foreseeable practical applications. Not only would the resin self-oxidize in presence of water to produce undesirable gassing, but this process wastes chlorine and appears to seal off the absorbed chlorine from normal use.

This instability problem raised the questions of why this chlorinated resin was unstable and under what conditions we can minimize the self-oxidation process. Therefore, the work in this thesis is mainly concerned with finding solutions to these questions. Two approaches were considered. The first deals with the problem of synthesis which was studied by Horning and Robertson⁴⁵. The second deals with the effect of changing conditions in the chlorination process. The results of the latter study provide the basis of this thesis.

Chapter Two

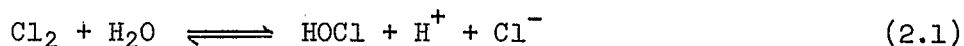
FACTORS INFLUENCING CHLORINATION

2.1 Introduction:

The chlorination of the UMF resin was assumed to be a critical step in the production of the proposed chlorinated resin. Of the factors involved, the chlorinating species, the chemical composition, and the physical structure of the resin are probably most important.

As the UMF resin may be used either for chlorine release or chlorine absorption, chlorine may simply be transferred from an aqueous chlorine solution directly into the resin according to equation (1.3). In fact, when the resin is exposed to a solution containing a high concentration of "active" chlorine, substantial amounts of chlorine will be absorbed very quickly, but it was observed that considerable decomposition of the resulting chlorinated resin can result. Therefore, chlorination with a much lower concentration is indicated although a longer reaction time will be required to achieve maximum loading. In addition to the concentration of active chlorine and time, other factors must be considered for chlorination of these resins, e.g., pH and temperature.

The change in pH value has an important effect on the chlorinating species. Thus, when chlorine (solution of chlorine gas or hypochlorite) dissolves in water it undergoes a very rapid hydrolysis to hypochlorous acid and hydrochloric acid:



The hydrolysis constant⁴⁶ of this reaction is 3.94×10^{-4} at 25°C. It may be seen from equation (2.1) that the concentration of HOCl depends on the total chlorine concentration and on the pH. In dilute solution and for pH-values greater than 4, the equilibrium shown in equation (2.1) is displaced to the right and very little Cl₂ exists in solution. This change is shown very clearly in the following table.²⁶

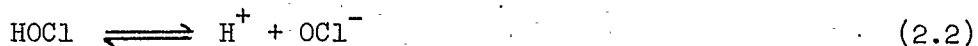
pH	10 ppm	100 ppm	1,000 ppm	5,000 ppm
1.0	96.5	73.7	21.8	(6.5) ^b
1.5	99.0	89.9	46.9	(18.2) ^b
2.0	99.6	96.5	73.7	41.2
2.5	99.9	99.0	89.9	69.0
3.0	99.96	99.6	96.5	87.5
3.5	99.99	99.9	99.0	95.7
4.0	99.99	99.96	99.6	98.5
4.5	99.99	99.99	99.96	99.5

Table 2.1 Percent of Total Available Chlorine Present in the Form of HOCl^a.

^a In an acid, aqueous chlorine solution at 25°C.

^b Values for solutions which would have more than 1 atm pressure of chlorine.

Above pH 5 the concentration of hypochlorite ion becomes appreciable, while that of molecular chlorine is negligible. Between pH 6.0 and 8.5, hypochlorous acid dissociates according to the following equation,

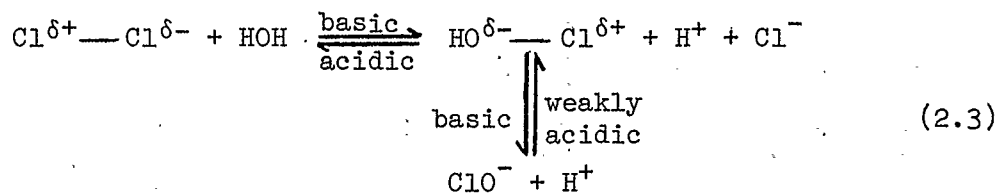


Thus, chlorine exists predominately as HOCl at low pH levels; concurrently, at 20°C above pH 7.5 and at 0°C above pH 7.8, hypochlorite ions (OCl⁻) predominate. Table 2.2 shows such change in the form of Cl* at various pH values.

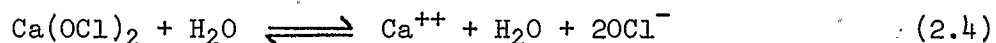
pH	As HOCl, %	pH	As HOCl, %
5.0	99.7	9.0	3.1
5.5	99.1	9.5	0.99
6.0	96.9	10.0	0.31
6.5	91.0	10.5	0.10
7.0	76.0	11.0	0.03
7.5	50.0	11.5	0.01
8.0	24.0	12.0	0.003
8.5	9.1		

Table 2.2 Percent of Total Chlorine in Hypochlorite Solutions Present as Hypochlorous Acid at Various pH levels, 25°C.

The following equation summarizes the variation of the form Cl* with changes in pH value:



When the chlorinating agent is calcium hypochlorite, $\text{Ca}(\text{OCl})_2$, or sodium hypochlorite, it ionizes in water to give hypochlorite ions:



The hypochlorite ions establish equilibrium with hydrogen ions, depending on pH as shown in equation (2.2).

Thus, the same equilibria are established in water regardless of whether elemental chlorine or hypochlorites are employed. The significant difference is in the resultant pH and its influence on the relative amounts of HOCl or OCl^- existing at equilibrium.

Sodium hypochlorite solution was used in this work as a chlorinating agent, since it was shown that the calcium hydroxide available contained some MnO_2 which in the chlorination process was converted to MnO_4^- as identified by U.V. absorption.

2.2 A General Account of the Probable Structure of UMF Resin:

Various formulations of urea-melamine formaldehyde resin have been developed in this study. Since the resins are insoluble, we can only speculate about the exact structure.

To be useful in the treatment of water, the resin must have an open structure such that the secondary amine groups are readily accessible both to take up chlorine and release it to water. Such resins have been termed "macro-reticular" by Dewar and Wayman¹⁶. Various proprietary⁴⁵ methods have been discovered by which this macro-reticular structure can be modified. These methods were not part of this study, and reference to the various modified resins will be made by code number only. The aim of this study was to discover the characteristics

of chlorination of a selected group of the modified UMF resins, and to study the stability of such resins. Resin 53-1 (Canadian Patent applied for, Robertson and Horning) was the basic polymer used in this study. Table (2.3) includes the formulations of different selected resins and its code number. The resins included in this table are basically 53-1 but changed as follows:

Code number	Content
53-1	Canadian Patent applied for, Robertson and Horning
144-1	Formaline (UMF) (Dewar resin)
144-2	modification of 53-1
144-3	increased pre-polymerization time. formaldehyde chain should be shorter
144-4	prepolymerized urea-formaldehyde.
144-5	UMF modification.
144-6	prepolymerized melamine formaldehyde.
144-7	modification of 53-1
144-8	53-1, no base added - strongly acidified

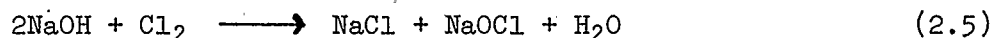
Table 2.3 Different formulations for chlorine exchange resin.

A detailed quantitative comparison was undertaken to assess the effect of changing different parameters during the chlorination process for all of the formulations mentioned in Table 2.3. The resins were.

treated in each run under conditions as nearly identical as possible.

2.3 A typical run of the chlorination process*:

A solution of sodium hypochlorite was prepared according to the equation:



The total concentration of the chlorine in solution was analyzed iodometrically to determine the concentration of chlorine at the beginning of the run. The NaOCl solution was constantly stirred in a 1/2 litre 3-necked flask and was left for at least 1/2 hour in a water bath adjusted to the desired temperature, until temperature equilibrium was reached.

A good quality of water free from oxidizable materials was used. The apparatus was covered with a black cloth to minimize chlorine decomposition. The pH of the solution was adjusted to the desired value by adding the required amount of HCl solution. In each study 5 g of the resin was added to the sodium hypochlorite solution, while at the same time the automatic timer-printer was activated. As soon as the polymer is introduced, it very rapidly adsorbs chlorine from the solution and at the same time, the pH value of the solution decreases due to the production of an acid grouping in the resin. To maintain the pH at the desired value during chlorination, an automatic titrator was used which delivered a standardized solution

* Details of the apparatus and experimental will be discussed in Chapter 4.

of 0.1M NaOH. This automatic syringe adds the required volume of sodium hydroxide incrementally on demand to restore the system to the desired pH value. This was achieved by the use of a pH meter in combination with a switching system (see Chapter 4). A calomel electrode was connected to a salt bridge containing KNO_3 solution while a glass electrode was immersed in the chlorinating medium. The automatic timer and printer recorded the number of counts of NaOH which was taken up to maintain a constant pH value at a certain time. After one hour of chlorination, 5 cc. of the solution was analyzed iodometrically to determine the concentration of free available chlorine in solution. At the same time, about 0.2 g of the chlorinated resin was removed, washed thoroughly, and air dried, to be used for the analysis of the combined available chlorine. The rest of the resin was left two hours in the chlorinating medium for further chlorination. After a period of three hours the automatic titrator was stopped, and the solution containing the resin was left overnight in the water bath for maximum loading. After a period of 24 hours, the resin was filtered from solution and washed thoroughly 3 to 4 times with doubly-distilled water to remove any excess chlorine on the surface of the resin. The resin was first air dried, then vacuum dried, and then was ready for stability tests.

2.4 Experimental Results:

The experimental work in this chapter deals primarily with four series.

2.4.1 Series 1

In this series the basic 53-1 resin (20-40 mesh) was treated at 10°C according to the typical run described above. Variations of pH, chlorine concentration, grain size, resin amount, presence of chlorate, chloride, and chlorite in the chlorinating medium have been considered.

a. Effect of pH

The pH may be considered as an important factor during the chlorination process. Three runs were done at pH 4, 5 and 6 to evaluate the effect of pH during chlorination of the resin. Table 2.4 shows the effect of changing pH on chlorine capacity of the resin, and the total amount of sodium hydroxide taken up during chlorination which we consider to be a measurement of the rate of oxidation of such a resin. It should be noted that the values of the analysis in Table (2.4) were taken after one hour of chlorination; also the initial chlorine concentration in each run was adjusted to be about the same (0.122 M).

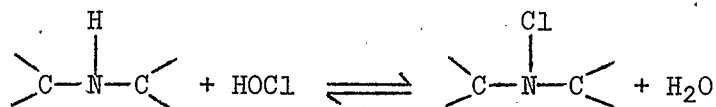
pH	mole/l free available Cl in soln after 1 hr.	mole/l NaOH after 1 hr.	wt % of Cl in the resin
4	0.046	0.0147	44.9
5	0.047	0.0139	42.0
6	0.052	0.0108	40.4

Table 2.4 *Effect of pH on chlorination of resin*

53-1 at 10°C.

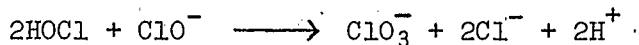
To explain the data in Table 2.4, let us consider the material balance. Chlorine can be used up according to the following reactions:

1. The chlorination of the resin which will use chlorine according to the usual equation (1.2)

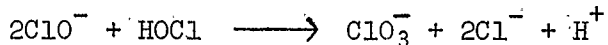


2. Oxidation: Some of the chlorine may be exhausted in the oxidation process in which acid is produced.
3. Condensation: Chlorine may be used up in the following reactions:

- a. Formation of ClO_3^- ions.



and

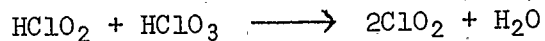
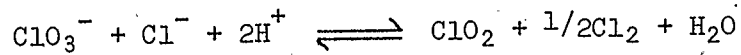


The first reaction⁴⁷ depends on the pH value, while the second reaction depends on the concentration of ClO^- . These reactions can only take place at high pH values (see Table 2.2).

Since this work was done in the range of pH 4-6, the possibility of exhausting some of the chlorine to form ClO_3^- was ruled out.

- b. Formation of ClO_2 :

chlorine could be used in the formation of ClO_2 according to the equations^{48,49,50}:



These reactions cannot take place unless we do have ClO_3^- ion in the solution. Thus, the possibility of using chlorine in the formation of ClO_2 was excluded.

Now, we have to consider the material balance on the basis that chlorine was mainly used for chlorinating the resin, while a lesser amount was used for oxidation.

From Table 2.4, starting with 0.122 molar active chlorine in one litre solution, after one hour of chlorination 0.046 M chlorine was left in solution, while 0.0147 M NaOH was consumed to balance the amount of acid produced during oxidation. The difference between the initial concentration of active chlorine (0.122 mole/l) and the residual (0.046 mole/l) will be equal to the concentration of chlorine used in step one and two. This was found to be consistent with assumed experimental error of about 1-2%.

It is obvious from Table 2.4 that the variation of pH in the range 4-6 has a slight effect on the total chlorine absorbed by the resin and the amount of resin oxidized to give acid. It is further noted that 5-6 times as much chlorine is adsorbed as disappears through oxidation of the resin.

In this study pH values ranging from 4-6 have been considered, since this resin was found to be more useful in this region¹⁶. Also, for values of pH greater than 7, especially 9-10, the chlorine is rapidly stripped from the chlorinated resin as hypochlorite, so chlorination under basic conditions is not feasible.

b. Effect of chlorine concentration:

5 g of the resin 53-1 (20-40 mesh) was chlorinated at 10°C and pH 4, using two different initial concentrations of "active chlorine" in solution.

Table 2.5 illustrates the effect of changing such concentration on the chlorine capacity of the resin.

initial concentration of active chlorine at time 0 (mole/l)	concentration of free available chlorine in solution after 1 hr.	mole/l NaOH after 1 hr.	wt % of Cl* in the resin
0.122	0.046	0.015	45
0.140	0.056	0.022	51
0.160	0.078	0.028	53

Table 2.5 Effect of active chlorine concentration on resin 53-1, chlorinated at pH 4 and 10°C.

It was observed that the resin absorbed substantial amounts of chlorine very rapidly from the stronger solution, but for the weaker chlorine solution, the resin reached its maximum chlorine capacity only after a longer period. This is not too surprising, although the observation may have practical value.

An indication of the rate of uptake is given in Table 2.6, where the variation of the chlorine capacity of the resin with time for adsorption from the stronger chlorine solution is illustrated.

Time in minute	Concentration of free chlorine in solution mole/l	wt % of combined chlorine in the resin. g Cl ₂ /g resin
0	0.158	--
5	0.120	25
10	0.097	28
20	0.085	42
60	0.078	53

Table 2.6 Variation of chlorine capacity of the resin with time, chlorinated at pH 4, 10°C, and initial Cl = 0.160 M.*

It is obvious that after 5 minutes of chlorination, the chlorine capacity of the resin was found to be 25% by weight. This is a remarkable value, since the maximum loading of the resin is only 30-40% by weight. After 20 minutes the resin used up about 40% of the initial chlorine and it achieved its final theoretical capacity (42%). At the same time as chlorine was being absorbed, a small number of groups in the resin were being more slowly oxidized, resulting in the evolution of gases. From these results, it was concluded that a lower chlorine concentration is better for chlorination, although a greater reaction time will be required to achieve maximum loading.

c. Effect of grain size:

Reference has already been made to the very rapid initial uptake of chlorine by the resin. This led to the question of whether

this was a surface effect or was related to a diffusion process. Further, there was the question of whether the oxidation step which was found to accompany chlorination was a surface effect or extended through the polymer. To find qualitative answers to these two kinds of questions, a series of chlorinations was carried out on resins of three different grain sizes. These sizes are 10-20 mesh, 20-40 mesh and 40-60 mesh.

Data resulting from a study designed to determine the effect of these grain sizes on the amount of chlorine taken up by the resin and the amount of NaOH consumed during chlorination, are collected in Table 2.7.

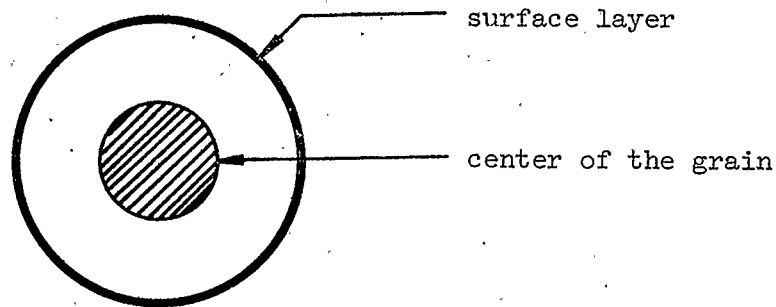
Grain sizes in mesh	mole/l free chlorine in solution after 1 hr.	mole/l NaOH after 1 hr.	wt % of the available combined chlorine in the resin after 1 hr.
10-20	0.043	0.0096	36
20-40	0.047	0.0139	42
40-60	0.040	0.0151	52

Table 2.7 Effect of grain size of resin 53-1 on the total amount of NaOH and the wt % of combined chlorine in the resin, chlorinated at pH 5 and 10°C.

It was found that the chlorine capacity of the resin and the total amount of sodium hydroxide, which appears to be related to the rate of oxidation of the chlorinated resins, could be represented by the following sequence.

10-20 mesh < 20-40 mesh < 40-60 mesh

If we represent the grain by the following diagram, it



is quite reasonable for the rate of chlorination to follow the above sequence, since for the larger grain size, chlorine will attack the surface of the grain and then takes longer time to penetrate the centre itself. In the meantime, for the finer grain size (40-60 mesh), it is easy for chlorine to diffuse from the surface to the core of the grain in a shorter time.

From the above discussion, we can conclude that the very rapid initial uptake of chlorine and the oxidation step which accompany chlorination are not a surface effect. The weight % of chlorine in the resin will achieve the same value whatever the grain sizes are, depending on the time of chlorination. Thus, the rates of absorption and liberation of available chlorine are governed by diffusion control rather than reaction control alone.

As a further check on this conclusion, three different amounts of the resin 53-1 ($2\frac{1}{2}$ g, 5 g & $7\frac{1}{2}$ g) were treated separately at 10°C and pH 5. The concentration of the initial available chlorine in the solution was about the same and the resin was treated in each run under conditions as nearly identical as possible. The results of such study are shown in Table 2.8.

Resin amount in gram.	mole/l free chlorine in solution after 1 hr.	mole/l NaOH after 1 hr.	wt % of chlorine in the resin after 1 hr.
2 ¹ / ₂	0.076	0.008	49.6
5	0.047	0.013	42.0
7 ¹ / ₂	0.0142	0.021	40.0

Table 2.8 Effect of the amount of resin on the wt % chlorine and the total amount of NaOH, at pH 5 and 10°C.

It was found that there is a linear relation between the amount of resin and the total concentration of sodium hydroxide consumed during the chlorination process which may be taken as an indication of oxidation as opposed to chlorine adsorption. The rate of chlorination was found to be proportional to the amount of resin in solution for a given initial concentration of active chlorine and the resin will be loaded to capacity, if there is enough chlorine in solution and enough time for maximum loading. These results again confirm the conclusion reached in the investigation of grain sizes.

d. Effect of added chlorite, chlorate and chloride ions on chlorination:

In our investigation, there was reason to believe that chlorite or even chlorate ions might be formed in the course of chlorinating the resins. Further, since it was shown that it was prefer-

able to use low concentration of active chlorine in the chlorination process, recirculation would consequently lead to a build-up of chloride ion concentration in the solution. Hence the effect of concentrations of ClO_2^- , ClO_3^- and Cl^- added to the standard chlorinating medium were investigated. It should be noted here that these experiments were merely exploratory.

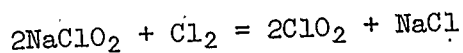
Effect of sodium chlorite:

Three experiments were carried out to investigate the effect of added chlorite ion. The first experiment was done using 5 g of 53-1 resin which was chlorinated in presence of 0.122 molar solution of active chlorine (ordinary run). The second experiment was carried out using $\text{NaClO}_2 + \text{NaOCl} + 5$ g of 53-1 resin. As a control, a third experiment was done to investigate the effect of sodium chlorite without the presence of the resin i.e. 1 g of NaClO_2 in 500 cc of NaOCl solution was used. The following Table summarizes the results of the three experiments.

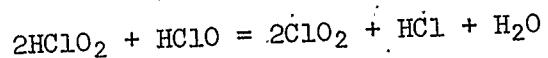
Run	mole/l residual chlorine in solution after 1 hr.	mole/l NaOH after 1 hr.	wt % of active chlorine in the resin.
$\text{NaOCl} + \text{resin}$	0.047	0.0139	42.0
$\text{NaOCl} + \text{resin} + \text{NaClO}_2$	0.042	0.0208	44.4
$\text{NaClO}_2 + \text{NaOCl}$	0.100	0.0170	--

Table 2.9 Effect of added chlorite on chlorination of resin 53-1 chlorinated at pH 5 and 10°C.

In the control experiment, when NaClO₂ was added to a solution of NaOCl, the HCl produced was balanced by the addition of a standard solution of 0.1 M NaOH to maintain a constant pH value (experiment three). This could be explained on the basis that in acid solution⁵¹ (pH 4-5), chlorine reacts with sodium chlorite nearly quantitatively according to the equation



Making allowance for the hydrolysis of chlorine, the same action for hypochlorous acid would be



When the resin was added to the chlorinating solution (NaOCl), it was found that there was a production of acid grouping in the resin due to oxidation which required 0.0139 M NaOH after 1 hour of chlorination.

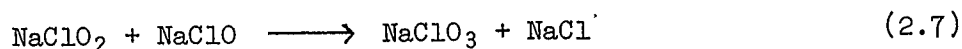
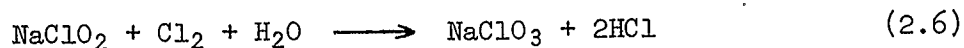
Now, the introduction of sodium chlorite into the solution of "active chlorine" in presence of the resin considerably increases the total amount of NaOH required to maintain a constant pH which we had previously assumed represents the amount of oxidation of the resin. The apparent weight % of active chlorine in the resin was increased by a small amount.

The increase of NaOH concentration taken up in experiment 2 may be due to the production of acid from the reaction of chlorite ion with hypochlorous acid and the oxidation of the resin during chlorination to produce acid grouping in the polymer chain.

Considering the material balance, starting with initial chlorine = 0.122 M, the concentration of NaOH = 0.0208 M, the residue of chlorine in solution was found to be = 0.042 M. The difference between the initial chlorine, the NaOH concentration and the residue of chlorine should be equal to the mole/l chlorine taken up by the resin, unless a reaction takes place in presence of ClO_2^- ion to produce another source of active chlorine on the resin.

It was found that the mole/l of active chlorine (0.0623) taken up by the resin was greater than the moles/l calculated according to the above discussion (0.059). There was a difference of 5.4% which is in agreement with the difference between the apparent wt % of the resin in the first and second experiments.

It is worth noting that chlorate ions can only be formed from the reaction of NaClO_2 with chlorine at pH 8 to 10 according to the following equations⁵²:



Under the experimental condition here (pH 5), the above reactions do not occur to a significant degree.

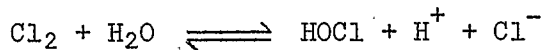
In conclusion, the introduction of ClO_2^- ions to the chlorinating medium produced a chlorinated resin with a slightly higher wt % active chlorine. It is noted that any loss of ClO^- to a higher oxidizable state should reduce the "active" chlorine available for chlorinating the resin, unless the product can also add to the secondary nitrogen.

Effect of chlorate:

It was found that the addition of KClO_3 to the chlorinating medium in absence and presence of the resin, hardly changed the amount of sodium hydroxide required to maintain a constant pH and hence did not change the degree of oxidation. The percentage of chlorine in the resulting resin also remained about the same. Hence, it was unlikely that appreciable amounts of chlorate would be formed under the chlorinating condition according to equations (2.6 and 2.7) and, if formed, would not affect the chlorination of the resin.

Effect of chloride:

In this study, 1 M solution of NaCl was introduced into the reaction mixture in presence of 5 g 53-1 resin at pH 5 and 10°C , to test the effect of a fairly large build up of this ion. It was noted that there was no remarkable change in the total amount of NaOH consumed. In spite of this fact, there was a considerable increase in the amount of gases evolved during the run. It is obvious from equation (2.1):



that the presence of 1 M Cl^- ion in a solution of 0.122 M NaOCl will have a significant effect on the balance of active chlorinating species.

In conclusion, the introduction of Cl^- ion to the solution of chlorine appears to accelerate the decarboxylation of the resin. Since approximately the same amount of NaOH is required, it would

seem that the addition of chloride ion brings about the oxidation of groups not touched under standard conditions.

2.4.2 Series 2 and 3:

The basic idea behind these two series of experiments was to study the effect of temperature on the behavior of the resin during the chlorination process. In both series most of the factors discussed in Series one were examined here, except that in Series two all the runs were done at 20°C while in Series 3, the temperature was raised to 40°C.

The data were collected in the following table to illustrate the effect of changing temperature.

pH	4			5		
	10	20	40	10	20	40
mole/l NaOH	0.0147	0.0180	0.0175	0.0140	0.0170	0.0199
mole/l free Cl ₂ in soln.	0.0470	0.0386	0.0151	0.0471	0.0380	0.0220
wt % of Cl ₂ in resin	40	47	48	41	48	51

Table 2.10 Effect of temperature on chlorination, at pH 4 and 5 grain size 20-40 mesh and initial Cl₂ = 0.122 M.

As shown in Table (2.10), raising the chlorination temperature from 10°C to 20°C and then to 40°C has a considerable effect

on the total amount of sodium hydroxide consumed during the reaction period, i.e., the rate of oxidation of the resin increased by raising the temperature. At a higher temperature, i.e., at 40°C remarkable amounts of gases were evolved. This may be due to the fact that higher temperature enhanced the decomposition of the most easily oxidizable parts of the chlorinated resin, and facilitated decarboxylation.

In conclusion, raising the temperature of chlorination resulted in about the same total active chlorine on the product (based on final, not initial, weight of resin), but there was a significant increase in the degree of oxidation. The resulting chlorinated resin showed a significant improvement in stability (see Chapter three).

2.4.3 Series 4:

In this series the question of whether the polymer composition has a considerable effect on the chlorination process, was considered. The different resins were formed from different proportions of the basic materials urea-melamine-formaldehyde, subjected to various purification, modification or proportion. The exact formulation lies outside the scope of this study. The resins used in this investigation were resins 144-1, 144-2, 144-3, 144-4, 144-5, 144-6, 144-7 and 144-8 (see Table 2.3). These resins were treated according to the typical run at pH 4, 20°C while using a grain size 20-40 mesh. Table 2.11 shows the data of such results.

Resin, code number	mole/l residual chlorine in solution	mole/l NaOH	wt % of the chlorine in the resin
53-1	0.0380	0.0180	46.5
144-1	0.0723	0.0103	27.2
144-2	0.0740	0.0102	42.4
144-3	0.0500	0.0145	45.2
144-4	0.0485	0.0140	48.1
144-5	0.0345	0.0208	45.4
144-6	0.0312	0.0175	33.6
144-7	0.0380	0.0170	53.0
144-8	0.0635	0.0133	44.6

Table 2.11 Effect of polymer composition on chlorination at pH 4, 20°C, initial Cl₂ = 0.0122 M and the results were taken after 1 hr. chlorination.

It is obvious that the modification of the structure of the basic resin 53-1 has a considerable effect on the concentration of sodium hydroxide taken up and also on the wt % of active chlorine in the resins. This effect is quite clear in resin 144-1 (Dewar's resin) and 144-6. Such changes in the formulation result in appreciable changes in the amount of NaOH used up, while the resulting resins contain comparable amounts of chlorine. The important practical difference, however, appears in the stability of the chlorinated resin.

2.5 Rate of Oxidation of Chlorinated UMF Resins:

During the chlorination of the resin, it was observed that a simultaneous oxidation of certain groups took place relatively easily. This fact is of considerable technical importance, since it reflects the internal structure of the resin and may be related to the stability of the resulting chlorinated resin.

Therefore, the rates of oxidation were determined during chlorination (in terms of acid production) for the resin 53-1 and other formulations under the conditions stated in Series 1, 2 and 3. The rate was determined by following the change in the concentration of NaOH consumed with time at constant pH.

It was found that the rate follows pseudo-first order kinetics. Logically the rate depends on the concentration of both the oxidizable groups present in the resin and on the concentration of available "active" chlorine. The term available active chlorine was introduced because, as will be shown, the major part of the oxidation takes place within the core of the resin. Hence the concentration of available chlorine may be quite different within the resin from that in the solution. Further, we know that there are groups which are relatively resistant to oxidation but which will react much more slowly than the groups attacked during the chlorination. The concentration of the former was neglected in this analysis.

If pseudo first order kinetics are followed, since the concentration of oxidizable groups decreases during chlorination, the concentration of chlorine must remain relatively constant. We know that the concentration of active chlorine in solution changed,

for example (Table 2.4, first experiment), from 0.122 molar to 0.046, hence there is a suggestion that the available concentration is diffusion-dependent. While this may be a factor particularly for larger grain sizes, another factor is likely to be responsible for the kinetic behaviour. Thus it was noted above that the major part of adsorption of chlorine took place in 5-10 minutes, dropping the concentration of the chlorine in solution to a lower value. This lower value then remained relatively constant and was larger than the concentration of oxidizable groups. This is why it was concluded that the reaction followed pseudo-first order kinetics after the initial absorption period was over. Toward the end of the reaction, in certain cases, deviation from first order kinetics was observed. In view of the complexity of the overall reaction, this is not surprising.

In a specific example where (a) is the concentration of sodium hydroxide after the reaction was complete and (x) is the concentration at time t, the total concentration of NaOH (a) is proportional to the total easily oxidizable groups, while (x) is proportional to the oxidizable groups at time t. Thus a plot of (t) against $\log \frac{a}{a-x}$ gave a straight line in which the slope is equal to the rate constant k_1 . The data necessary for such a plot were derived from the information given in the following tables. These data were taken for the resin 53-1 at pH 5 and 10°C using a grain size 20-40 mesh, also for the same resin at 40°C and pH 4.

Time in minute	# of counts of NaOH	mole/l NaOH (x)	$\log \frac{a}{a-x}$
6.66	4667	0.0073	0.3290
8.75	5206	0.0082	0.3895
14.01	5980	0.0094	0.4938
18.56	6592	0.0104	0.5986
24.98	7201	0.0114	0.7344
35.04	7856	0.0124	0.9571
44.32	8270	0.0130	1.1907
48.06	8435	0.0132	1.3392
52.60	8545	0.0134	1.5782
57.65	8845	0.0139 (a)	--

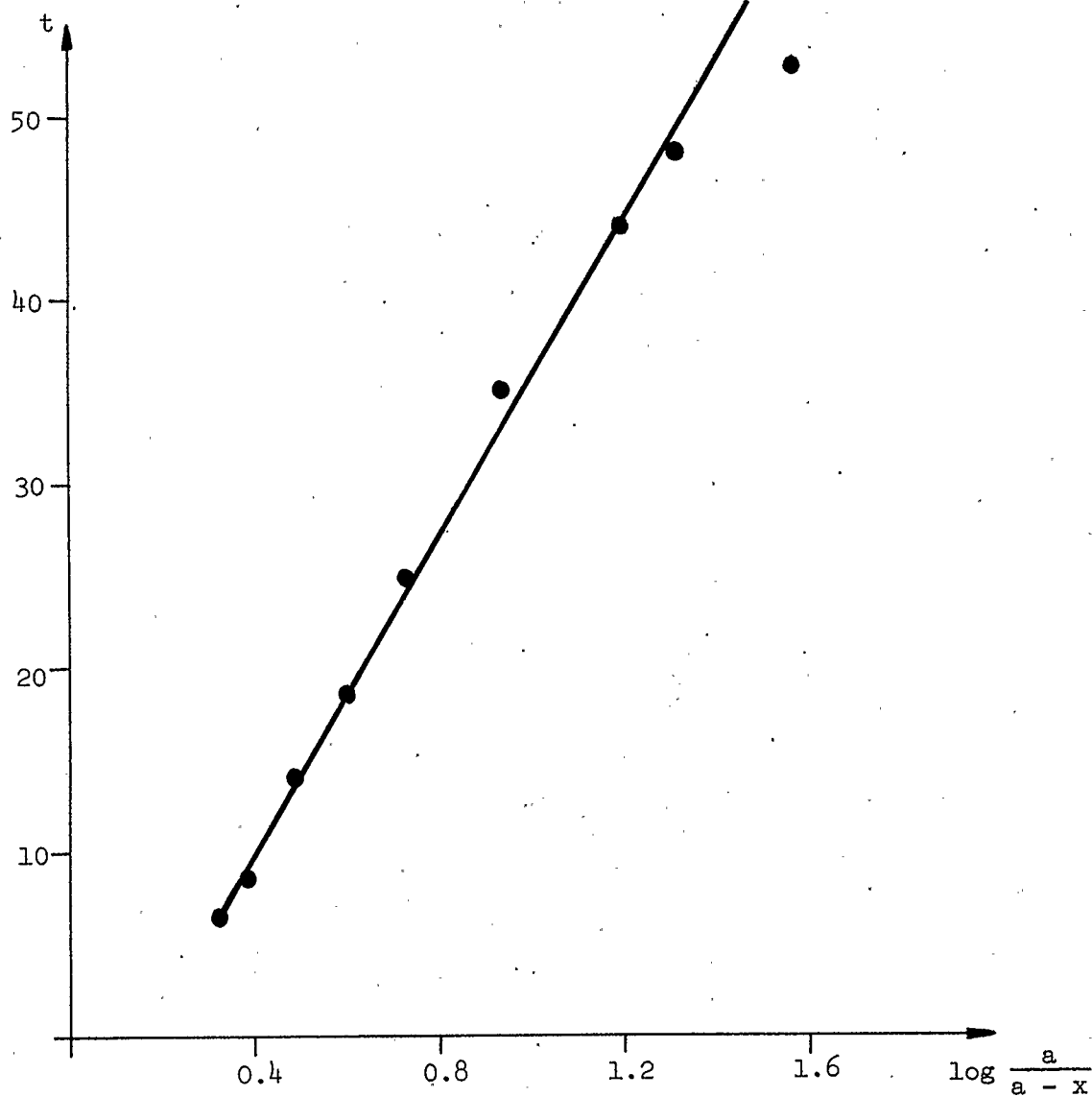
Table 2.12 Data for determining the rate of oxidation of resin 53-1 at pH 5 and 10°C. Initial $Cl_2 = 0.122 M$

Time in minute	# of counts of NaOH	mole/l NaOH (x)	$\log \frac{a}{a-x}$
3.48	5027	0.0078	0.1936
6.00	6025	0.0094	0.2942
9.2	6882	0.0107	0.3567
12.26	7570	0.0118	0.4177
22.2	8787	0.0136	0.5486
28.40	9425	0.0146	0.6346
34.60	10032	0.0156	0.7369
41.98	10412	0.0162	0.8186
46.3	10662	0.0165	0.8762
51.01	10902	0.0169	0.9386
59.46	11271	0.0175	1.0769
69.21	11612	0.0180	1.2436
91	12358	0.0191	--

Table 2.13 Data for determining the rate of oxidation of resin 53-1 at pH 4 and 40°C. Initial Cl₂ = 0.122 M.

The plot of such data resulted in a straight line relation as indicated in Fig. 2.1 and 2.2.

It has been noted that the rate of oxidation increases by raising the temperature. Such an effect is shown in Table 2.14.



*Fig. 2.1 Rate of oxidation of resin 53-1 chlorinated
at 10°C and pH 5.*

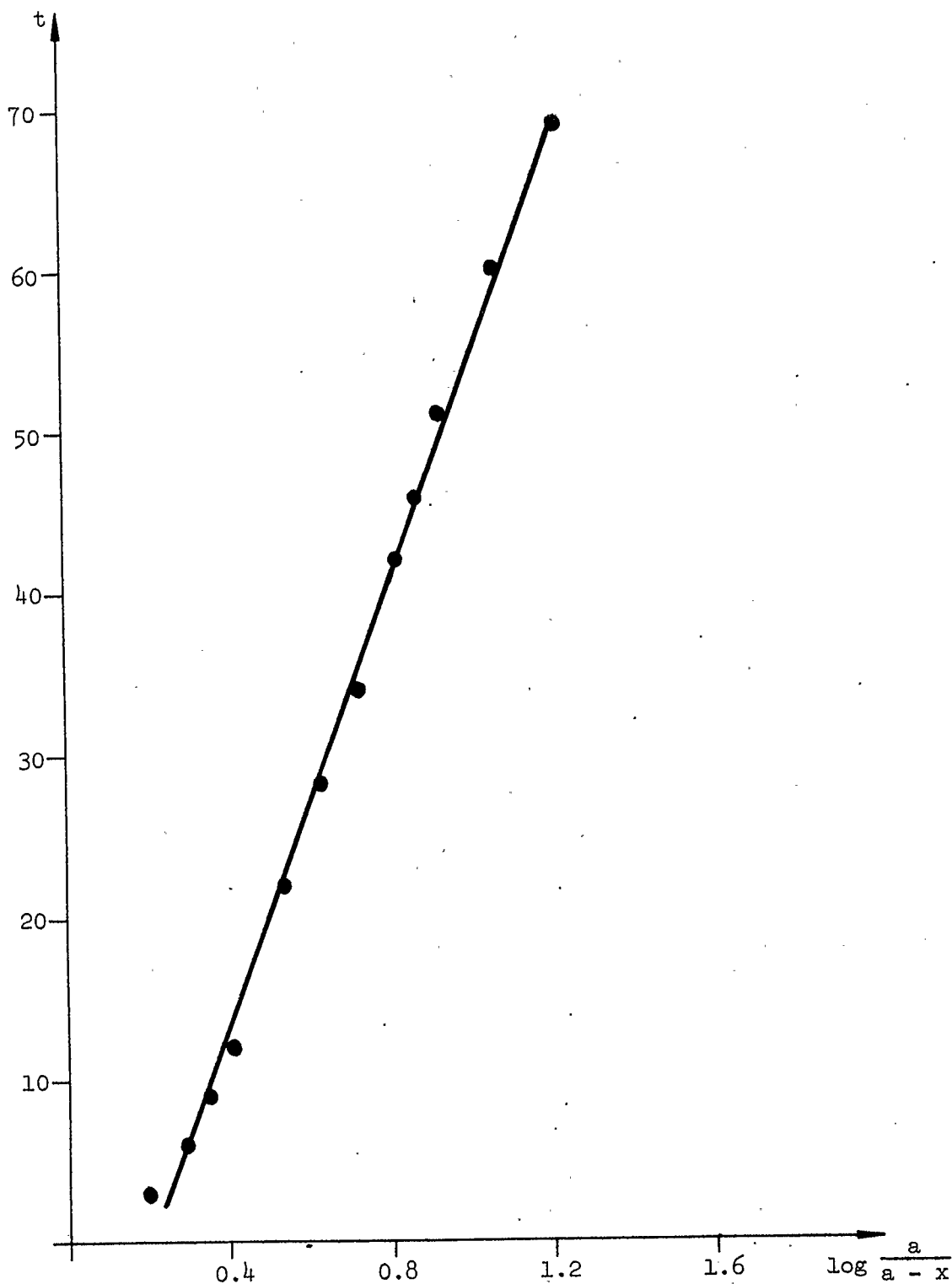


Fig. 2.2 Rate of oxidation of resin 53-1 chlorinated at pH 4 and 40°C.

Temperature in C°	$k_1 \text{ min}^{-1}$
10	44.39 ± 0.5
20	47.00 ± 0.7
40	75.33 ± 0.6

Table 2.14 Effect of different temperature on the rate of oxidation for resin 53-1 at pH 5.

As the temperature increases, the probability of more resistant groups that can be oxidized increases. Therefore, at 40°C we have a mixture of groups which can be readily oxidized. Also, by increasing the temperature, there is a considerable activation energy for the more difficult group, because at 10°C these barely react, while at 40°C they react more easily. Since different groups are involved, no simple activation energy can be estimated from the above data.

Polymer composition could also affect the rate of oxidation because the concentration of the oxidizable groups is probably different from one resin to another, depending on the structure of the resins. Table 2.15 shows the effect of polymer composition on the rate of oxidation.

Resin code number	$k_1 \text{ min}^{-1}$
53-1	43.99 ± 0.8
144-1	77.32 ± 0.5
144-2	58.78 ± 0.3
144-3	67.80 ± 0.4
144-4	66.89 ± 0.5
144-5	68.79 ± 0.6
144-6	62.11 ± 0.3
144-7	62.72 ± 0.7
144-8	59.79 ± 0.6

Table 2.15 Effect of different compositions of UMF resin on the rate of oxidation, chlorinated at 20°C and pH 4.

2.6 Conclusion:

In this chapter we have investigated the various factors which influence the chlorination process of the basic resin urea-melamine-formaldehyde for different formulations. It was found that the variation of the pH in the range (4-6) has a slight effect on the total chlorine absorbed by the resin and the amount of resin oxidized to give acid. In the investigation of the effect of the initial chlorine concentration, it was found that the rate of chlorination and of oxidation of the resin is related to the initial chlorine concentrations; higher concentrations accelerate the

oxidation of the easily oxidizable group in the resin during the chlorination process. But higher concentrations may lead to undesirable oxidation. Therefore, a lower concentration is better for chlorination although a greater reaction time will be required to achieve maximum loading. The grain size of the resin was observed to have a great effect on chlorination. It was found that the rates of absorption and liberation of available chlorine are governed by diffusion control rather than by reaction control alone. This fact was confirmed by using different amounts and grain sizes of the resin. Also, while the effect of added chlorite ions to the chlorinating medium produced a chlorinated resin with slightly higher wt % active chlorine, this did not seem to introduce an important change. The introduction of Cl^- and ClO_3^- to the chlorinating solution has no effect on the NaOH consumption or chlorine absorption, except that there was a production of gases in the case of adding chloride ion.

Raising the temperature was found to increase the total degree of oxidation and the resulting chlorinated resins showed a significant improvement in stability. Changes in polymer composition produce significant differences in the chlorinated resin both with respect to oxidation in the chlorination process under the actual conditions, and in stability. The rate of oxidation of the chlorinated 53-1 resin and other formulations was studied; it was found that the rate of the reaction follows a pseudo first-order kinetics. The rate of oxidation increases by raising the temperature, and it is different for the different formulations of the basic 53-1 resin. A significant activation energy for the oxidation reaction cannot be calculated.

Chapter Three

STABILITY OF CHLORINATED UMF RESINS

3.1 Introduction:

In the chlorination studies of urea-melamine-formaldehyde resin discussed in Chapter 2, it was found that there are certain groups in the resin which can be relatively easily oxidized. This tendency to oxidation and particularly to self-oxidation under normal usage in water purification, creates a major problem associated with such chlorinated polyamide resins. Since the same basic constituents were used in all UMF resins, differences in ease of oxidation must be related to the structure. The structure of urea-formaldehyde or melamine-formaldehyde resins (Section 1.1.2), were assumed to contain groups of the form $[-NH-CH_2-NH-]$. These, we believed to be easily oxidizable, at least in certain configurations.

In general, most polyamide resins show such a tendency to autoxidation. The rate and course of these oxidation reactions have been shown to be strongly affected by light, heat, oxygen concentration, moisture, and the presence of trace impurities which can act as either catalysts or inhibitors (antioxidants)⁵³. Most of these polymers will show both chain scission and chain crosslinking on autoxidation. Generally, one reaction will predominate over the other so that either the polymer will show a pronounced decrease in molecular weight and be converted to low molecular weight residues, or the polymers will show a pronounced increase in this property to the point that insoluble, infusible crosslinked products are formed.

Self-oxidation is familiar³⁷ in the yellowing of cottons treated with polyamide type resins (in early wash-and wear type) and exposed to chlorine bleaches in washing processes. This defect eliminated this particular group for this application. Similarly this is claimed to be the cause of deterioration of untreated nylon rope used about salt water.

This effect of self-oxidation is quickly self-evident when chlorinated polyamides derived from urea-formaldehyde or urea-melamine-formaldehyde are used in treating water supplies. The resins are unstable to greater or lesser degree in a static water system. On standing only a few hours, some resins will begin evolving gaseous products (carbon dioxide, and nitrogen, primarily) in significant quantities. This gas production not only creates undesirable gassing, but wastes chlorine⁴⁵ and appears to seal off the residual absorbed chlorine from normal use.

From the above observations, it is obvious that the self-oxidation of the chlorinated UMF resin represents a serious problem with respect to its application in water purification. Therefore, the work in this chapter will attempt to shed light on this problem from the point of view of gas production from the resin 53-1 and other formulations under various conditions. Also reference will be made to a special method of chlorination, which produced a remarkable reduction in the instability of such resins.

3.2 Measurements of Self-oxidation of Chlorinated Polyamide Resins

Under Various Conditions:

In order to compare the stability of chlorinated UMF resin

and other formulations, a simple testing system has been developed in which the resin was submerged while the self-oxidation of such chlorinated resins was measured by measuring the amount of gas released at room temperature from equal weights of the resins immersed in water.

A comparison of the gas release rates of 1 g samples of the basic 53-1 resin and the 144-1 resin (prepared according to Dewar method) is given in Table 3.1 and shown graphically in Fig. 3.1. These resins were chlorinated at 20°C and pH 4 under conditions as nearly identical as possible.

Relative Volume of Gas in mm for a Cross Section = $\frac{\pi \times (12)^2}{4}$ mm ² at 1 atms.		Time (days)
53-1	144-1	
12	14	5
22	29	10
30	45	15
41	63	20
52	--	25

Table 3.1 Comparison of the gases released from 1 g of resin 53-1 and 144-1 chlorinated at pH 4 and 20°C.

It is obvious that resin 53-1 is somewhat more stable than resin 144-1. Since we believe that $(-\text{NH}-\text{CH}_2-\text{NH}-)$ group is the more easily oxidizable group, therefore a production of a resin which

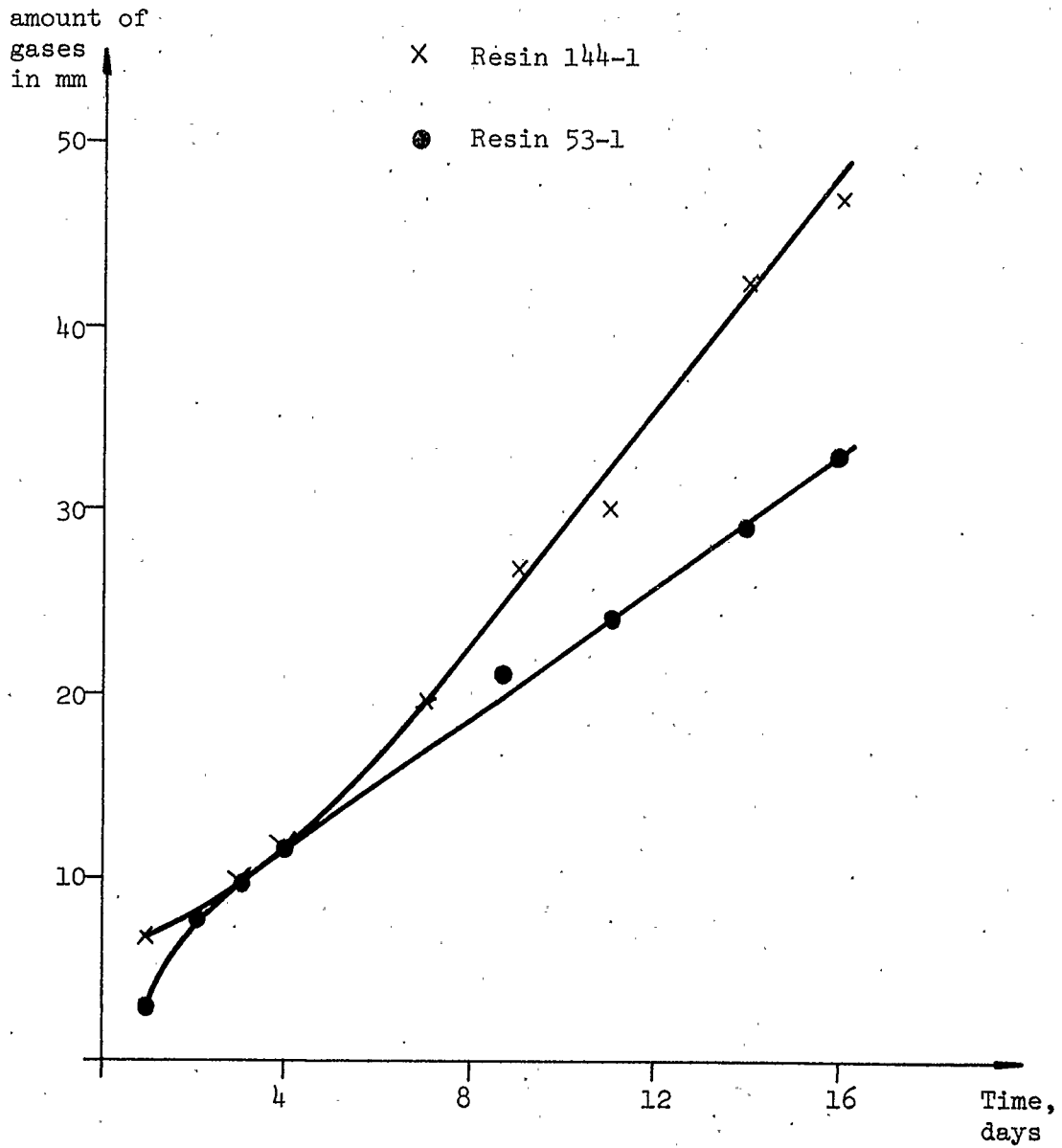


Fig. 3.1 The amount of gases released from resins 53-1 and 144-1 chlorinated at pH 4 and 20°C.

reduces the presence of such oxidizable groups in the polymer chain results in a relatively more stable chlorinated resin. This may be the reason for the greater relative stability of resin 53-1 compared to 144-1 resin⁴⁵ but this has not been proved since, both are insoluble, cross-linked resins.

The effect of changing the structure by variation in the proportion and conditions of polymerization of the basic UMF resin and the method of chlorination was found to have a great effect on the stability of such chlorinated resin. These differences are indicated in Table 3.2, Fig. 3.2 and Fig. 3.3.

Resin	Relative Volume of Gas after 10 days:
53-1	22
144-1	29
144-2	75
144-3	12
144-4	21
144-5	29
144-6	27
144-7	23
144-8	12

Table 3.2 Comparison of the gas evolution from resin 53-1 and 144 series chlorinated at pH 4 and 20°C.

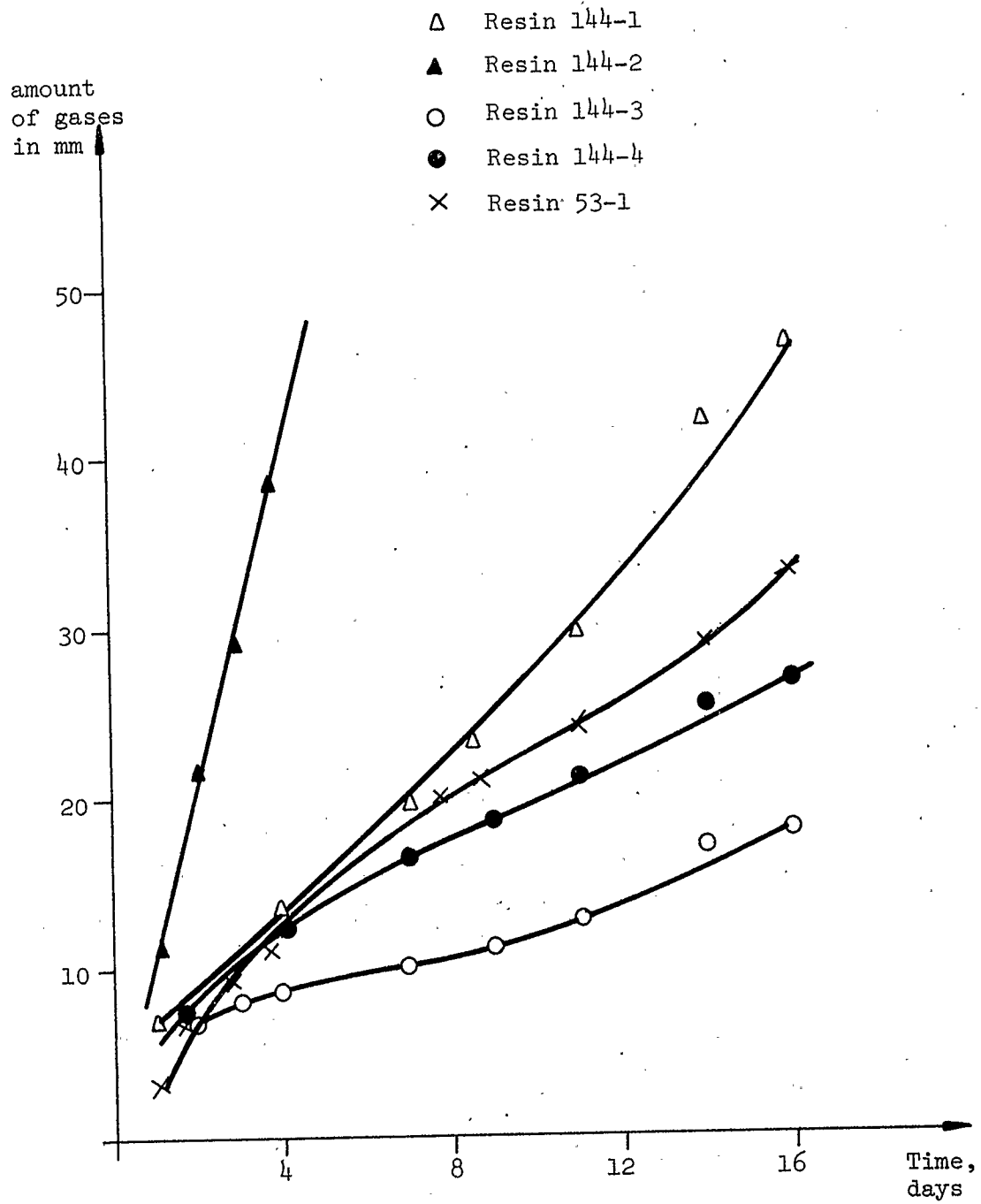


Fig. 3.2 The amount of gases released from resins 53-1, 144-1, 144-2, 144-3 and 144-4 chlorinated at pH 4 and 20°C.

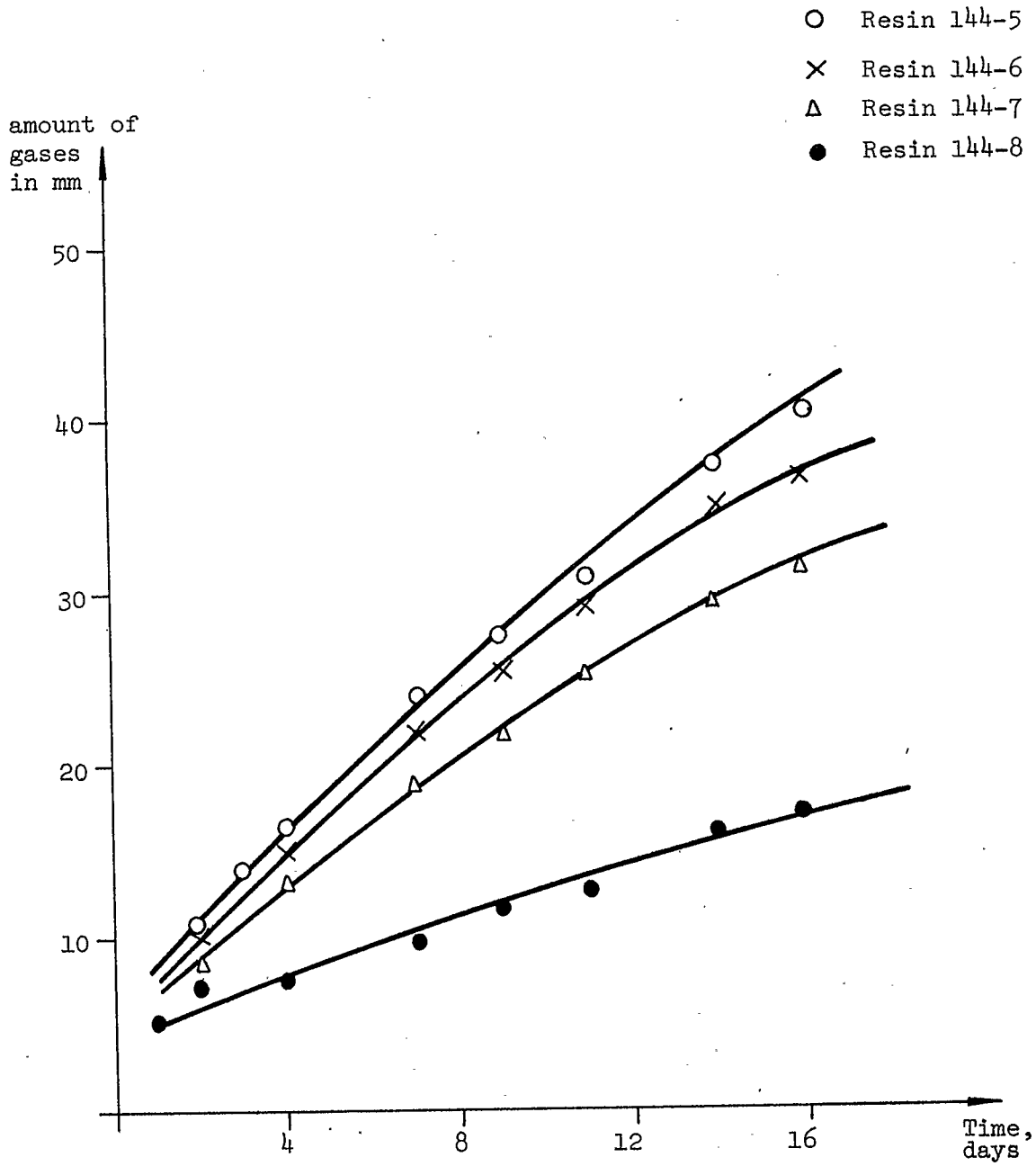


Fig. 3.3 The amount of gases released from resins 144-5, 144-6, 144-7 and 144-8 chlorinated at pH 4 and 20°C.

While it is difficult, if not impossible, to characterize the above resins by usual polymer techniques due to the insoluble, infusible cross-linked nature, this does not exclude the conclusion that structural differences do exist and these are related to the differences evident in Table 3.2.

One of the more important factors studied in Section 2.4.2 was the effect of different temperatures on the chlorination process. This factor was found to have a considerable effect on the stability of chlorinated UMF resins. The resin which was chlorinated at higher temperature (40°C) was found to be more stable relative to that which was chlorinated at 10°C. This fact could be explained on the basis that at 10°C the oxidation of only the relatively easily oxidizable groups took place while at 40°C oxidation of both the more resistant and easily oxidizable groups occur. These expectations were confirmed as shown in Table 3.3 and Fig. 3.4.

Temperature of chlorination, °C.	Relative Volume of Gas after 10 days.
10	75
20	44
40	14

Table 3.3 Effect of different temperatures of chlorination on the stability of the resin 53-1 at pH 5.

In addition to improvements in the stability of UMF resins to self-oxidation achieved through modification in the structure of

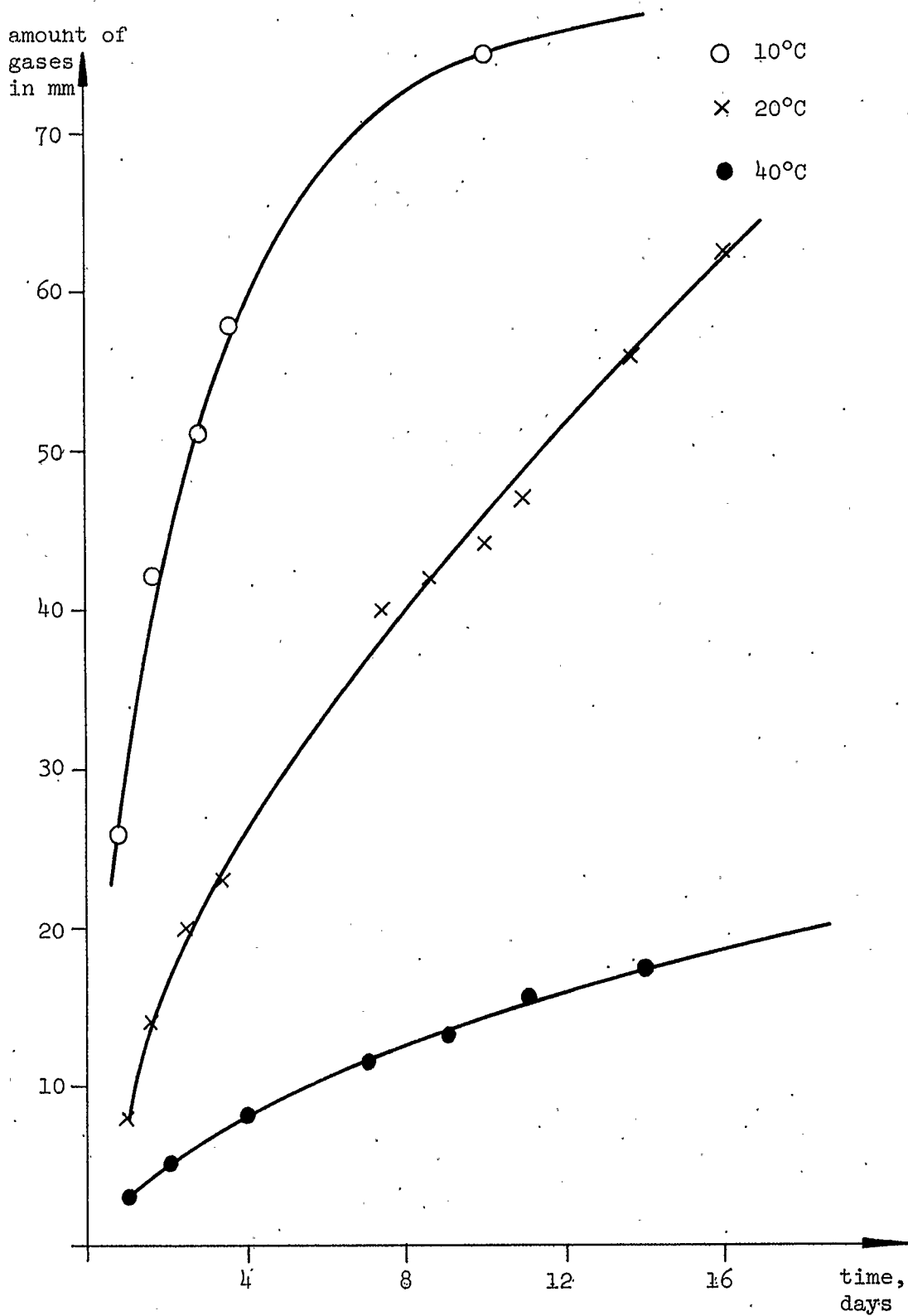


Fig. 3.4 The amount of gases released from resin 53-1 chlorinated at pH 5 and different temperatures.

the resin, it was found that a remarkable improvement in stability can be obtained by using a special procedure of chlorination. This procedure was a development based on the above observation.

3.3 Multiple chlorination process:

The basic idea behind the multiple chlorination process is that, after a preliminary chlorination, the chlorinated resin was induced to oxidize those easily oxidizable groups by heating for varying periods of time depending on temperature and then re-chlorinating.

In the first chlorination step, the resin was suspended in water with vigorous stirring and slowly bubbling chlorine gas through the suspension. The pH of the solution was adjusted between (4-5), first by adding acetic acid to the solution which makes the lower pH easier to hold by addition of calcium hydroxide. The resin was chlorinated for a period of three hours at room temperature. The chlorinated resin is then washed and heated up to about 80°C. After about 30 minutes a noticeable decomposition begins to occur during which excessive frothing may occur. The reaction was controlled by cooling the solution to hold the temperature at $\approx 80^{\circ}\text{C}$. After heating for an hour, a sample of the chlorinated resin was tested for residual chlorine. It was found that the chlorine content is usually reduced to only a few percent. The chlorinated resin was finally rechlorinated according to the typical run given in Section 2.3.

Resins 53-1, 144-2, 144-4, 144-6 and 144-7 were chlorinated according to the multiple chlorination process to investigate the effect of this modified method of chlorination mainly on the stability

of such chlorinated resins.

In the prechlorination process, the resins were chlorinated at pH 4 and 20°C using grain size (20-40) mesh and initial Cl₂ = 0.122 M. The results of such prechlorination are indicated in Table 3.4.

Resin	mole/l NaOH after 1 hr.	mole/l residual chlorine in solution after 1 hr.	wt % of available chlorine in the resin
53-1	0.0250	0.0241	52.2
144-2	0.0270	0.0161	57.6
144-4	0.0286	0.0168	54.1
144-6	0.0188	0.0458	54.5
144-7	0.0196	0.0374	54.6

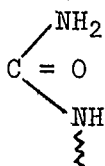
Table 3.4 Wt % of chlorine in the prechlorinated resins, at 20°C and pH 4.

The above results were surprising in that the resins on analysis gave over 50% chlorine. On the basis of the assumed structure of urea-formaldehyde (Section 1.1.2), only about 28% by weight chlorine can be held. Since some proportion of melamine was necessary in order to obtain the proper physical characteristics of the polymer, the presence of this component will necessarily increase the overall chlorine content (37%) compared to the urea-formaldehyde structure shown before. Since the addition of melamine to the resin will provide only a small increase in the chlorine content in the resin,

another explanation must be found for the unexpected high values of chlorine content shown in Table 3.4.

There are several possibilities which may explain this over 50% by weight chlorine in the resins. These possibilities are as follows:

1. The presence of ClO_3^- , ClO_2^- and/or ClO_2 introduced into the analysis of positive chlorine in the resin. As explained before in Section 2.4.1, these ions hardly exist under our experimental conditions and therefore, can be ruled out as an explanation.
2. The possibility of primary amine groups from urea partially incorporated with the resin structure.



3. The formation of primary amide end groups during the oxidation process. This seems to be the most likely possibility as will be shown in Section 3.5.

These resins which were subjected to the multiple chlorination, were found to be more stable relative to the same resins which were chlorinated according to the ordinary chlorination process. This improvement in stability is quite obvious in Table 3.5, Fig. 3.5 and Fig. 3.6 which include a comparison between the resins chlorinated according to ordinary and multiple chlorination.

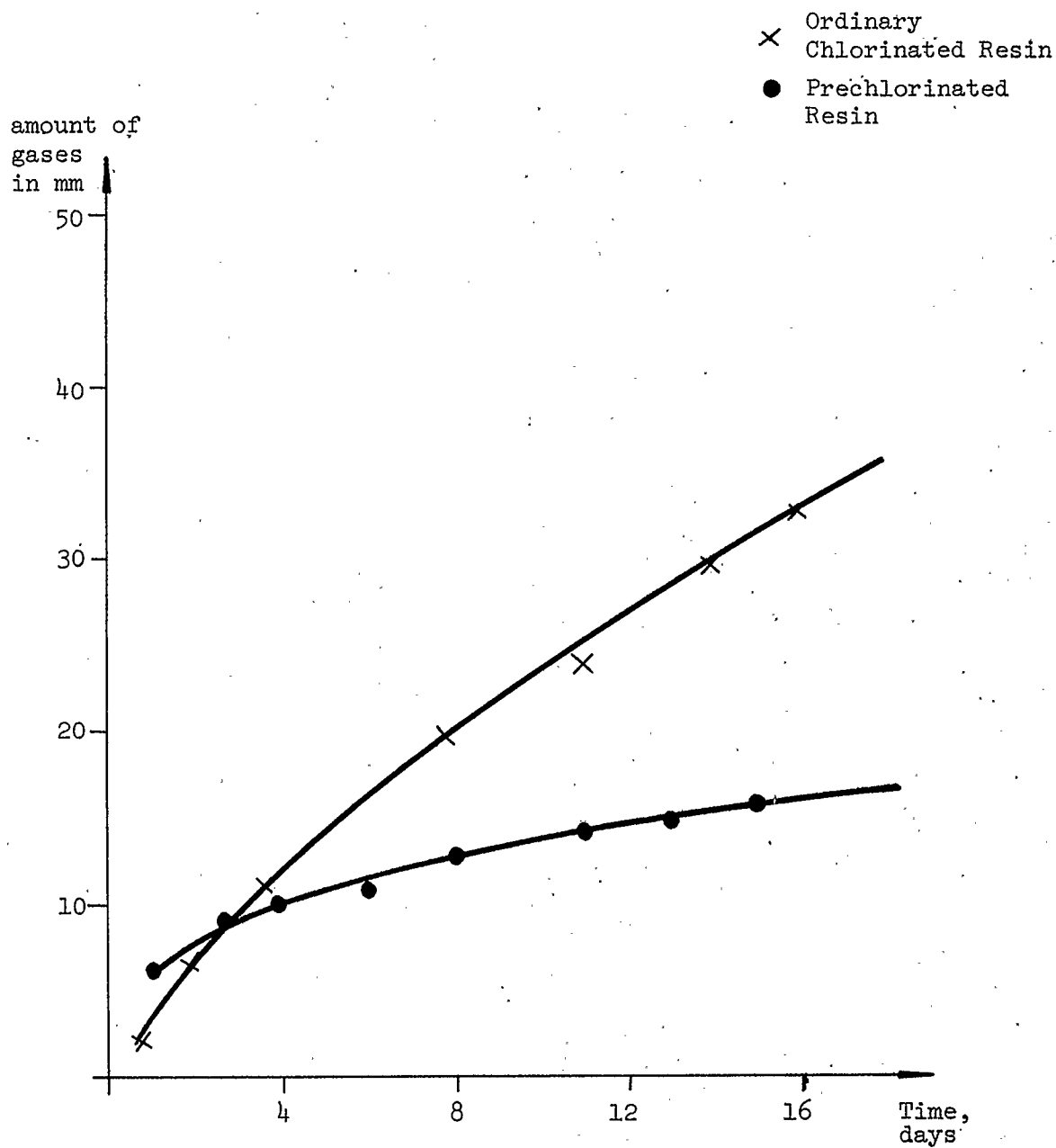


Fig. 3.5 The amount of gases released from resin 53-1 chlorinated according to both ordinary and multiple chlorination processes at pH 4 and 20°C.

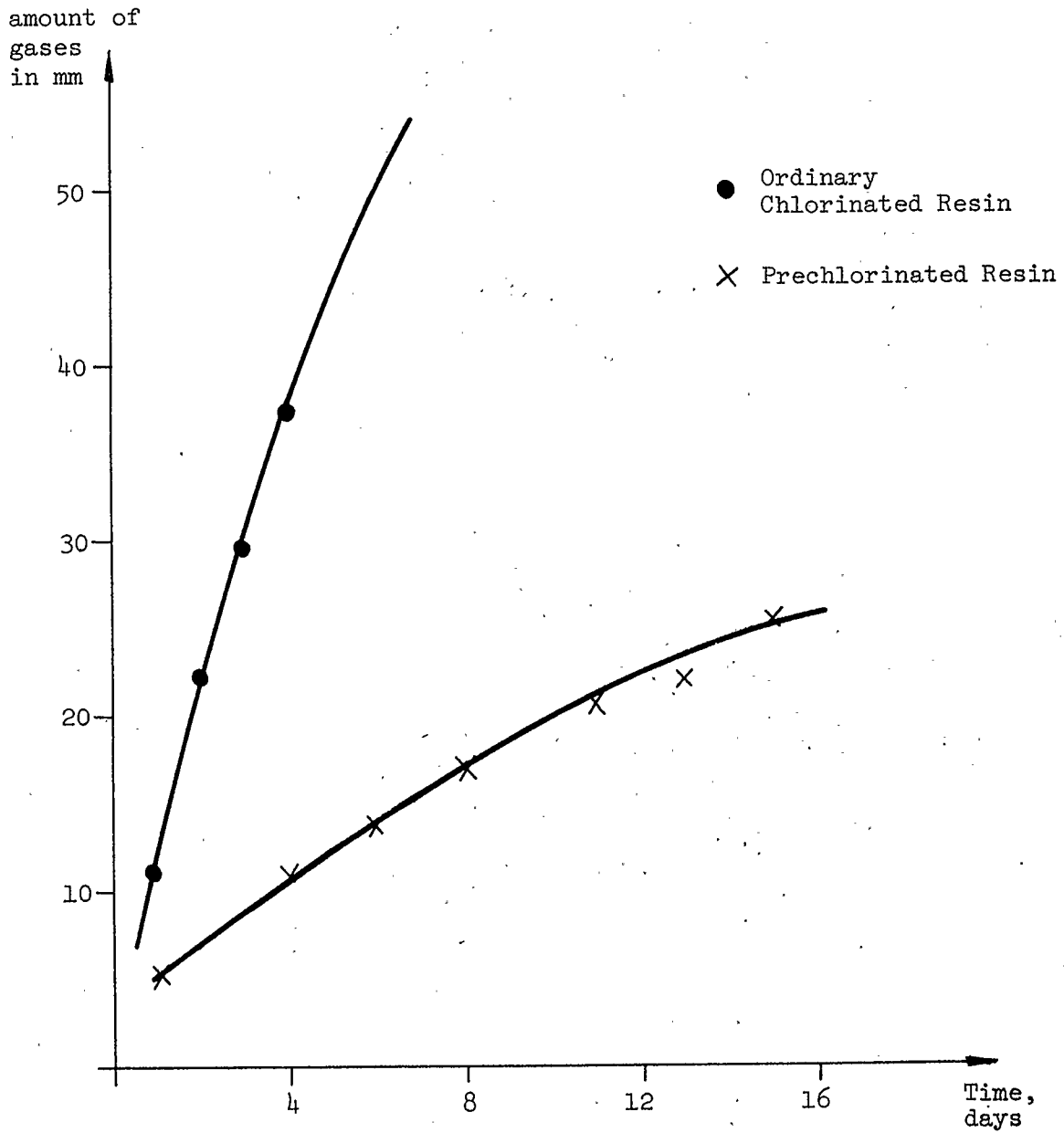


Fig. 3.6 The amount of gases released from resin 144-2 chlorinated according to both ordinary and multiple chlorination processes at pH 4 and 20°C.

Resin	Relative volume of gas after 15 days.	
	ordinary chlorination	multiple chlorination
53-1	31.5	15.5
144-2	> 75.0	25.5
144-4	25.5	12.0
144-6	35.0	17.0
144-7	30.0	19.0

Table 3.5 Comparison of the gases released from the resins chlorinated according to both ordinary and multiple chlorination.

From these results it could be concluded that the multiple chlorination method was a successful method for improving the stability of chlorinated polyamides since it removes most of the easily oxidizable groups.

3.4 Gas analysis:

The gases produced as a result of self-oxidation of chlorinated 53-1 resin and other formulations under various conditions were analyzed using the mass spectrometer. It was found that the gases evolved during the self-oxidation process were essentially carbon dioxide, nitrogen, oxygen and a small amount of carbon monoxide. The mass number at $m/e = 28$ was separated to give mainly nitrogen

with traces of carbon monoxide. The percentage of the relative intensity of such gases for a specific example using resin 53-1 which was chlorinated at pH 6 and 10°C is illustrated in Table 3.6. The peak at $m/e=28$ which corresponds to nitrogen was considered as the base peak.

m/e	Gas	% of relative intensity
44	CO ₂	10.0
28	N ₂	47.8
32	O ₂	19.0
28	CO	5.8

Table 3.6 % of relative intensity of the gases evolved from resin 53-1 chlorinated at pH 6 and 10°C.

The percentage of carbon dioxide gas relative to the total amount of gases was calculated to be 58%; this is probably low. The percentage of nitrogen was 28% while carbon monoxide and oxygen were found to be present in a small amount, 11.0% and 3% respectively.

Another example of gas analysis is given in Table 3.7 for resin 144-3 chlorinated at 20°C and pH 4. The results confirm the order of the relative amounts of gases found in the previous example.

Gas	% of the gas relative to the total gases
CO ₂	57
N ₂	23
O ₂	17
CO	3

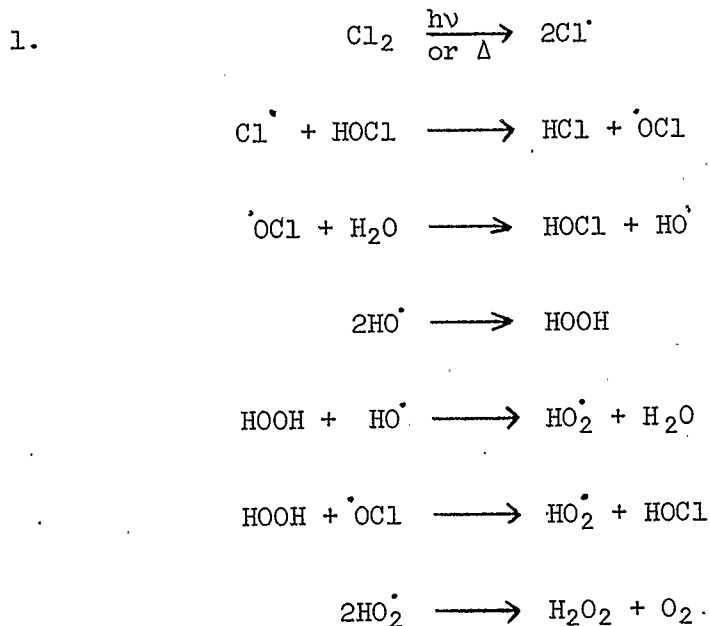
Table 3.7 % of the gases evolved from resin 144-3 chlorinated at pH 4 and 20°C.

3.5 A Hypothesis for the Mechanism of Self-oxidation of Chlorinated Urea-melamine-formaldehyde Resins:

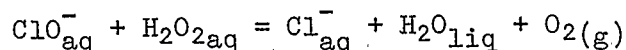
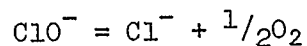
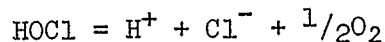
From our previous studies, the problem of self-oxidation of chlorinated urea-melamine-formaldehyde resins led us to propose the following mechanism for the self-oxidation process. The basis of this hypothesis is derived from the mechanism proposed for the oxidation of simple aliphatic model amides given by Sharkey and Mochel⁵⁴. This mechanism was also adopted by Kroes and co-workers^{55,56} and more recently by Mikolasewski and et al⁵⁷ for polyamides. The hypothesis is based on a free-radical mechanism. No low molecular weight chlorinated residues were found in our system, hence the reduction of active chlorine must lead to the formation of other oxidizing agents presumably involving oxygen. The nature of the products depends on the relative immobility of the activated ends⁵⁶. Sharkey and Mochel showed that the oxidation proceeds principally by rupture of the bond between the nitrogen of the amide and the

carbon of its α -methylene group for model compounds and it has subsequently been shown to occur similarly for polyamides^{55,56}.

Possible sources of the oxidizing agent in our chlorinated UMF resins are as follows:



2. In the presence of HOCl as a chlorinating agent using cobalt oxide as a catalyst, Flis⁵⁸ showed that the main oxidizing processes are due to the effect of oxygen. Solution of HOCl and ClO^- when irradiated produce oxygen according to the reactions^{59,60}.



Under our experimental conditions, it is likely that mechanism (1) represents the main source of the oxidizing agent.

Some qualitative experiments were carried out to test this hypothesis.

(a) Effect of light:

If the reaction mechanism involves a free-radical processes, it will be expected that the reaction will be initiated more readily in the presence of light than in the dark. Two experiments were carried out to investigate the effect of light on the gas evolution. In the first experiment, 1 g of 53-1 resin chlorinated at pH 5 and 20°C was tested for gas evolution in the presence of sun-shine. As a control, a second experiment was carried out in the dark using the same resin. It was found that the amount of gases evolved in presence of light is 5 times the amount in the dark. This proves that light can act as an initiator to form the free radicals but does not exclude a "dark reaction". Table 3.8 shows the amount of gases evolved in these experiments.

Time (in hr.)	Relative volume of gas	
	In light	In dark
0.08	8	0.0
0.2	15	6
24	44	9
48	63	15
68	>75	19

Table 3.8 Effect of light on the evolution of gases from resin 53-1 chlorinated at 20°C and pH 5.

(b) Addition of antioxidants:

Another exploratory experiment on the free-radical mechanism is the use of antioxidant^{61,62} which apparently act by decomposing any peroxide formed. The same type of resin mentioned above, chlorinated under the same conditions, was tested for gas evolution using three type of antioxidants, α -naphthol, β -naphthol, and hydroquinone. As a control another experiment was carried out using the same resin in water alone. It was found that in the case of α and β -naphthol, the amount of gases evolved was reduced to a remarkable degree as shown in Table 3.9. However, this may have been caused by reduction in Cl* content through direct action with chlorine. For this reason two other experiments were carried out, using the unchlorinated resin, in water with and without α -naphthol. It was found that the unchlorinated resin still can

Time (hr.)	Relative Volume of Gasses			
	plain	α -naphthol	β -naphthol	Hydroquinone
43	18	2	3	5
63	22	5	5	6
83	23	6	6	9

Table 3.9 Effect of added antioxidant to resin 53-1 chlorinated at pH 5 and 20°C.

self-oxidize to give off gases but with a slower rate compared to the same chlorinated resin. The addition of antioxidant prevents the evolution of gases. This suggests that the reaction is a free-radical one, involving peroxide as oxidizing agent. It should be noted that both the above two experiments were carried out in presence of light.

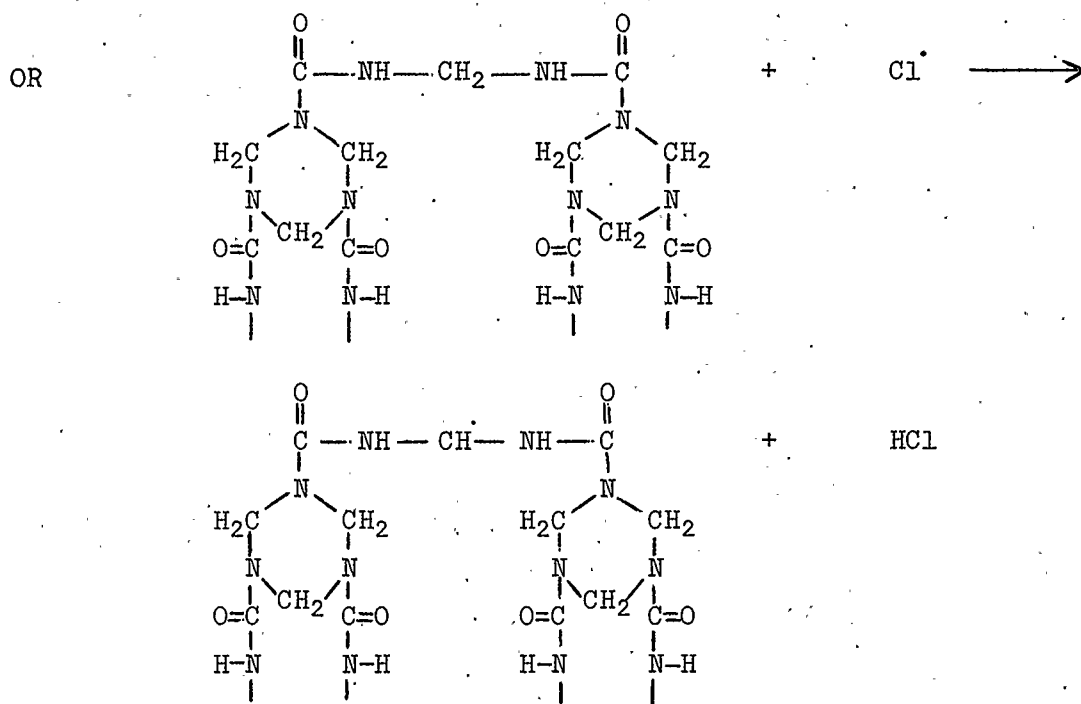
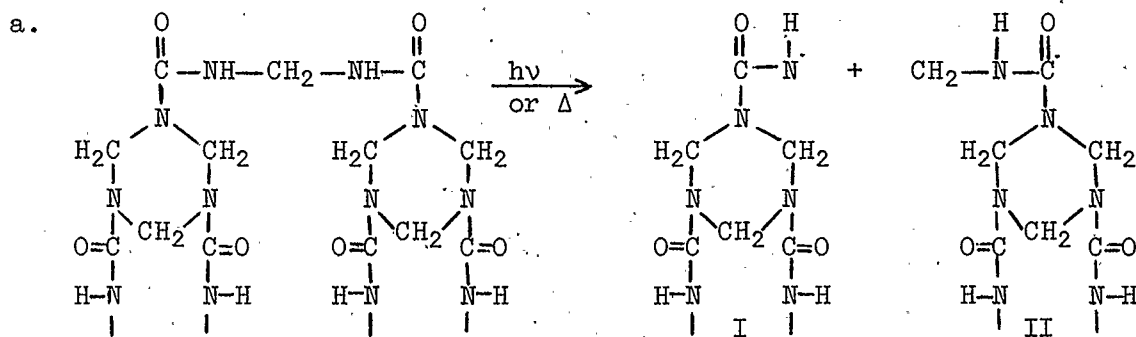
(c) Addition of hydrogen peroxide:

If the reaction mechanism is free-radical involving hydrogen peroxide as a very active oxidizing intermediate, it will be expected that the addition of H_2O_2 to the system will initiate the reaction readily. This was found to be true with the same chlorinated resin using a very dilute solution of H_2O_2 . The oxidation reaction was very fast and more than 75 mm of gases were evolved within 2 minutes. The same experiment was carried out using the unchlorinated resin in presence of H_2O_2 . It was observed that the unchlorinated resin undergoes self-oxidation too, but with a slower rate compared to the

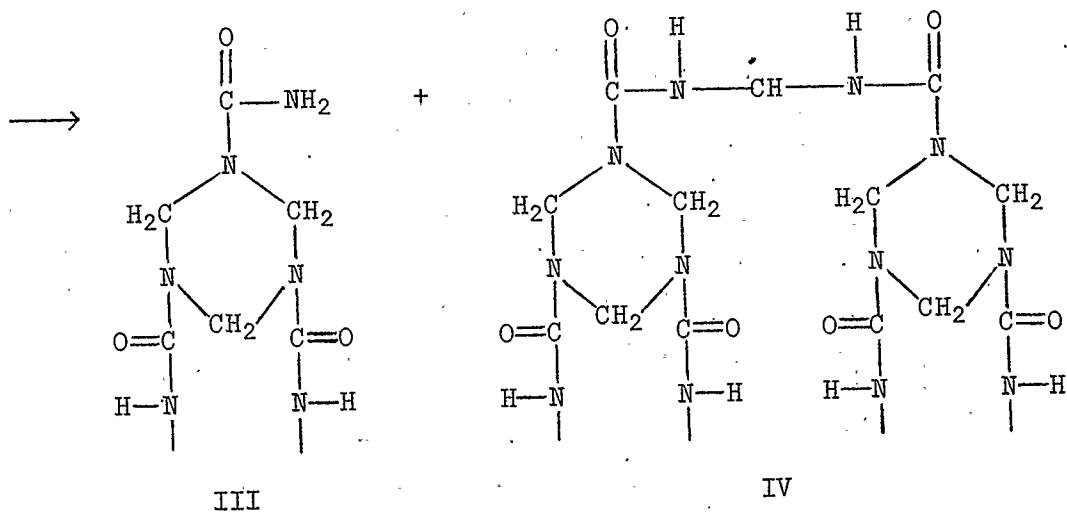
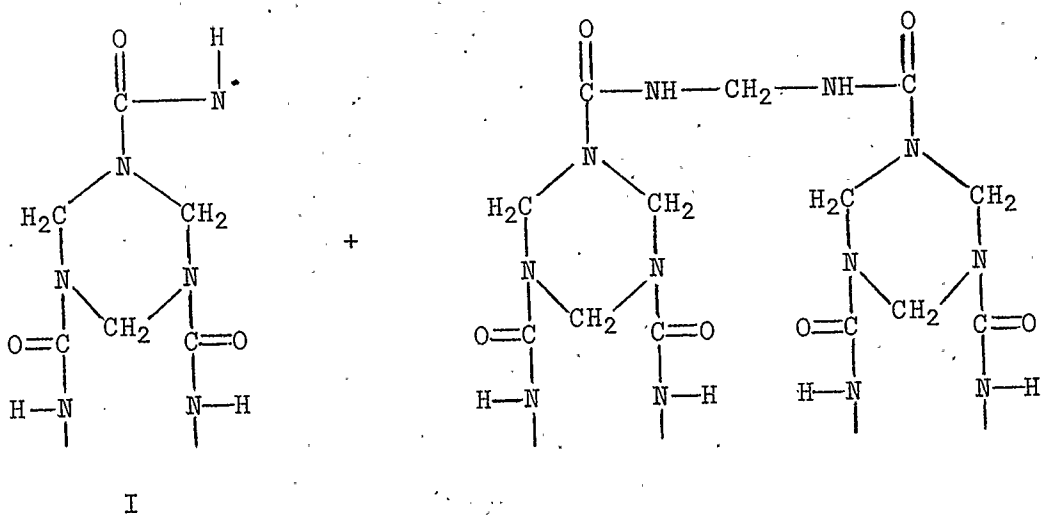
chlorinated one. It is worth noting that the gases evolved in both cases were analyzed, and were found to be CO₂, N₂, O₂ and CO.

It is suggested that the mechanism of self oxidation consists of the following steps:

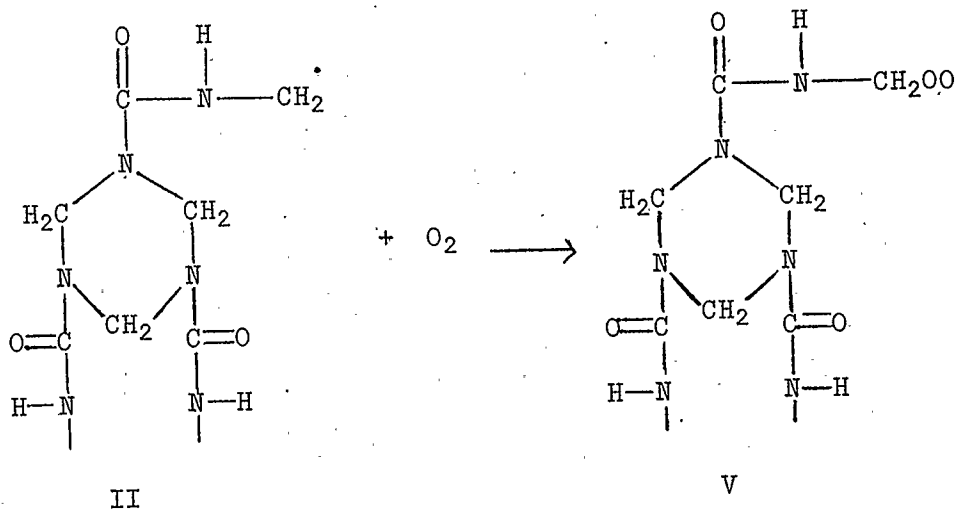
I Primary initiation cycle:



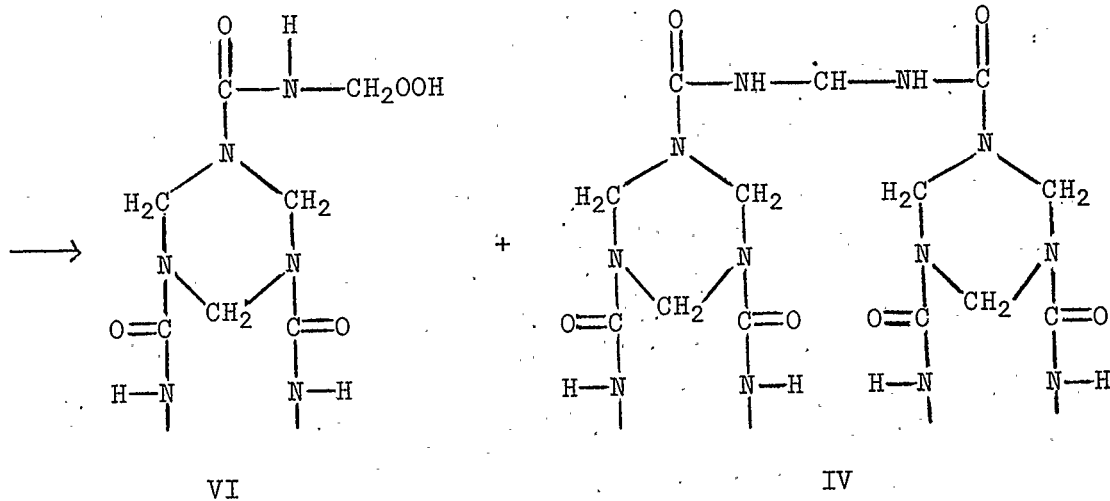
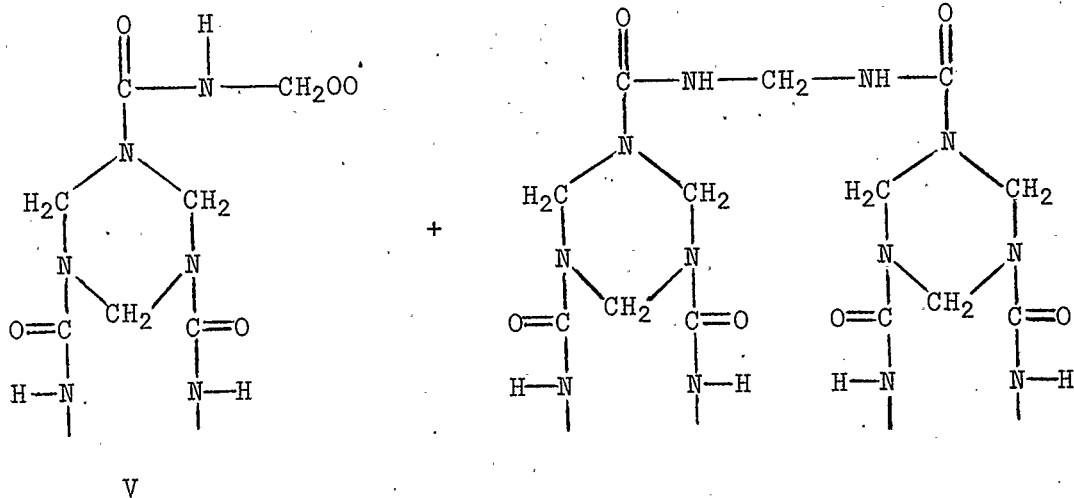
b.



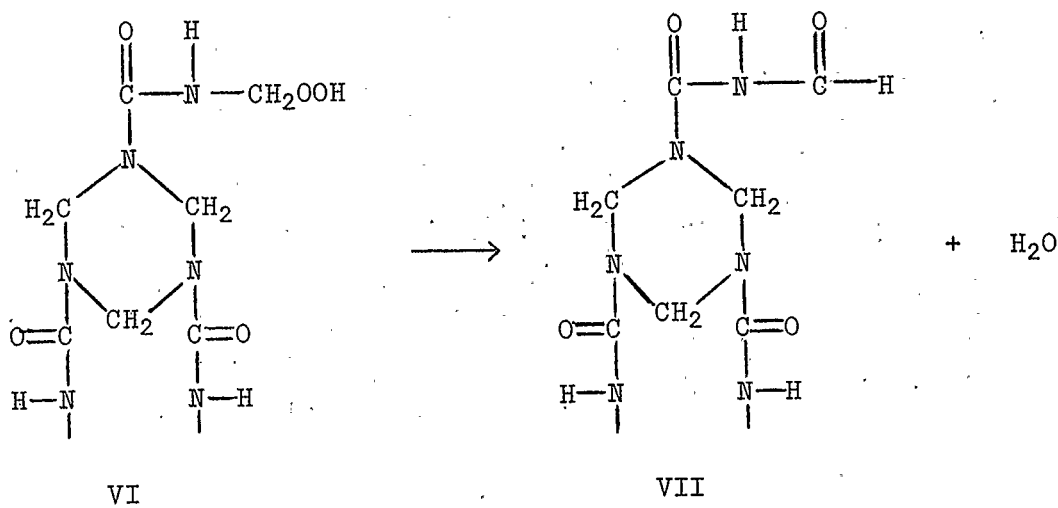
c.



d.

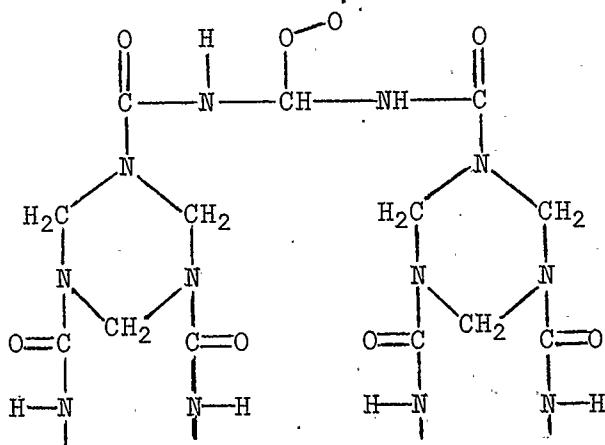
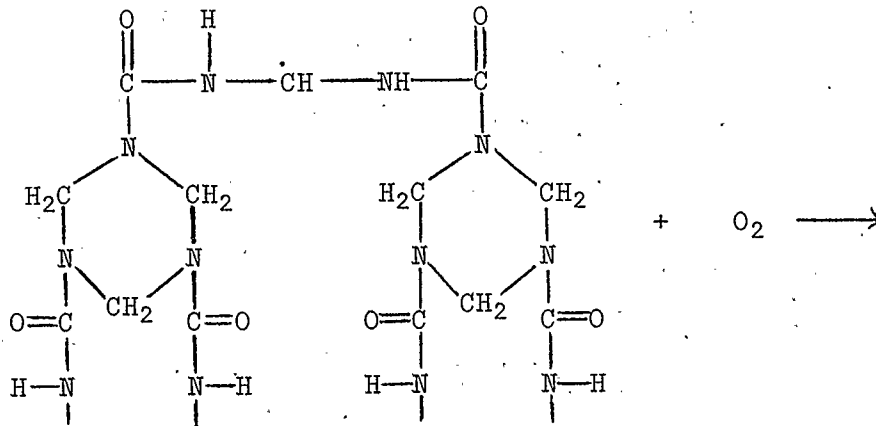


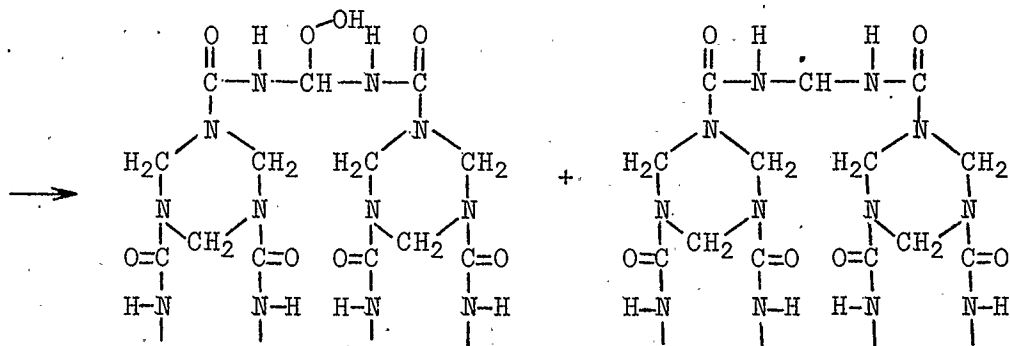
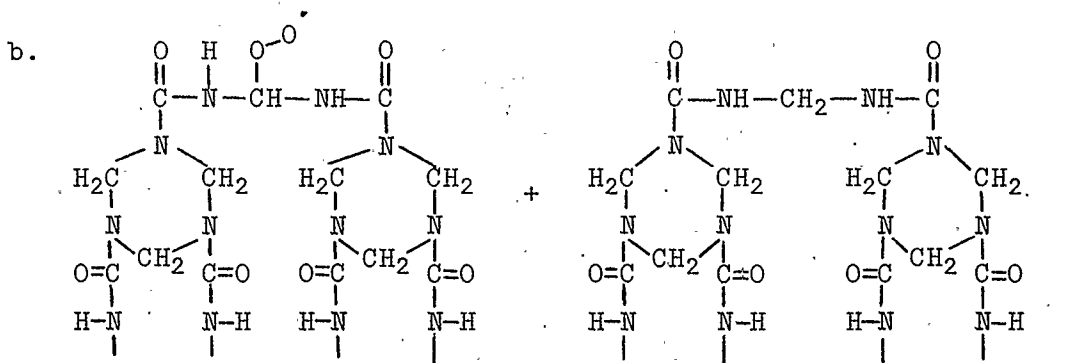
e.



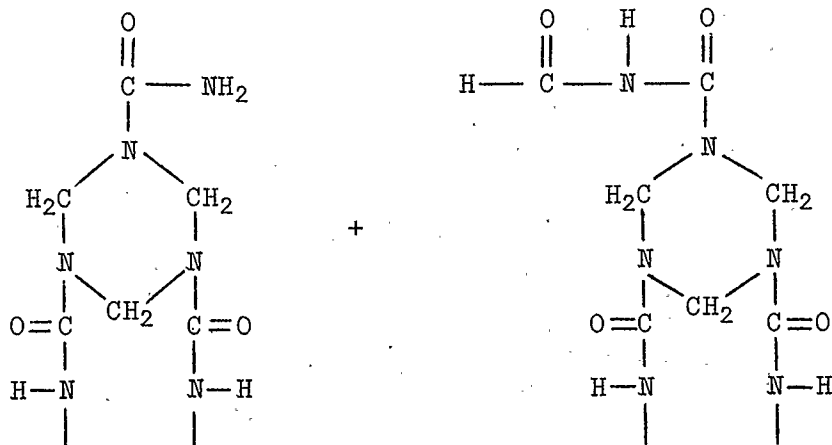
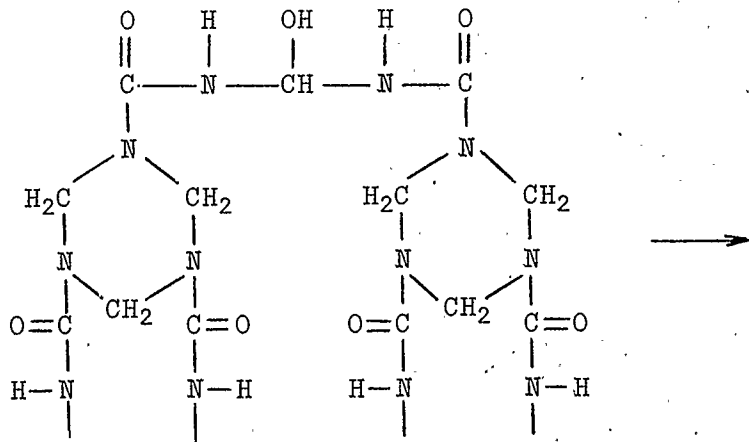
II Propagation followed by rupture of the chains:

a.

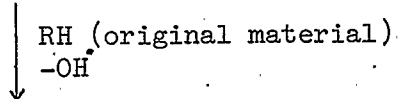
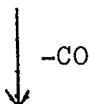
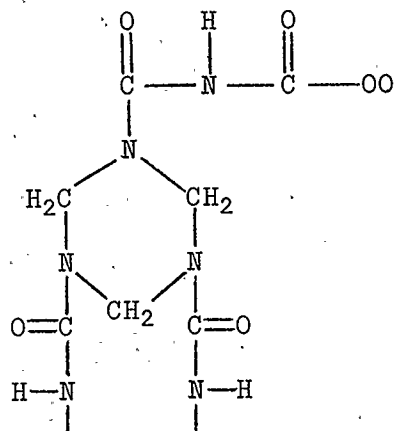
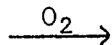
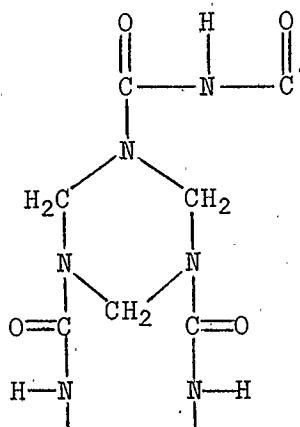
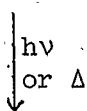
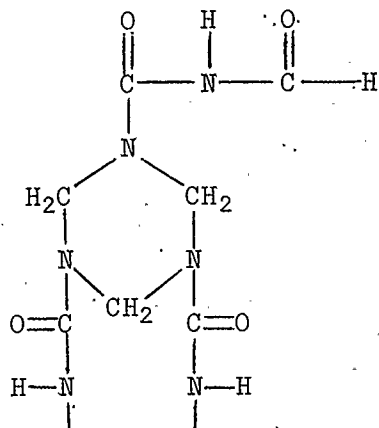


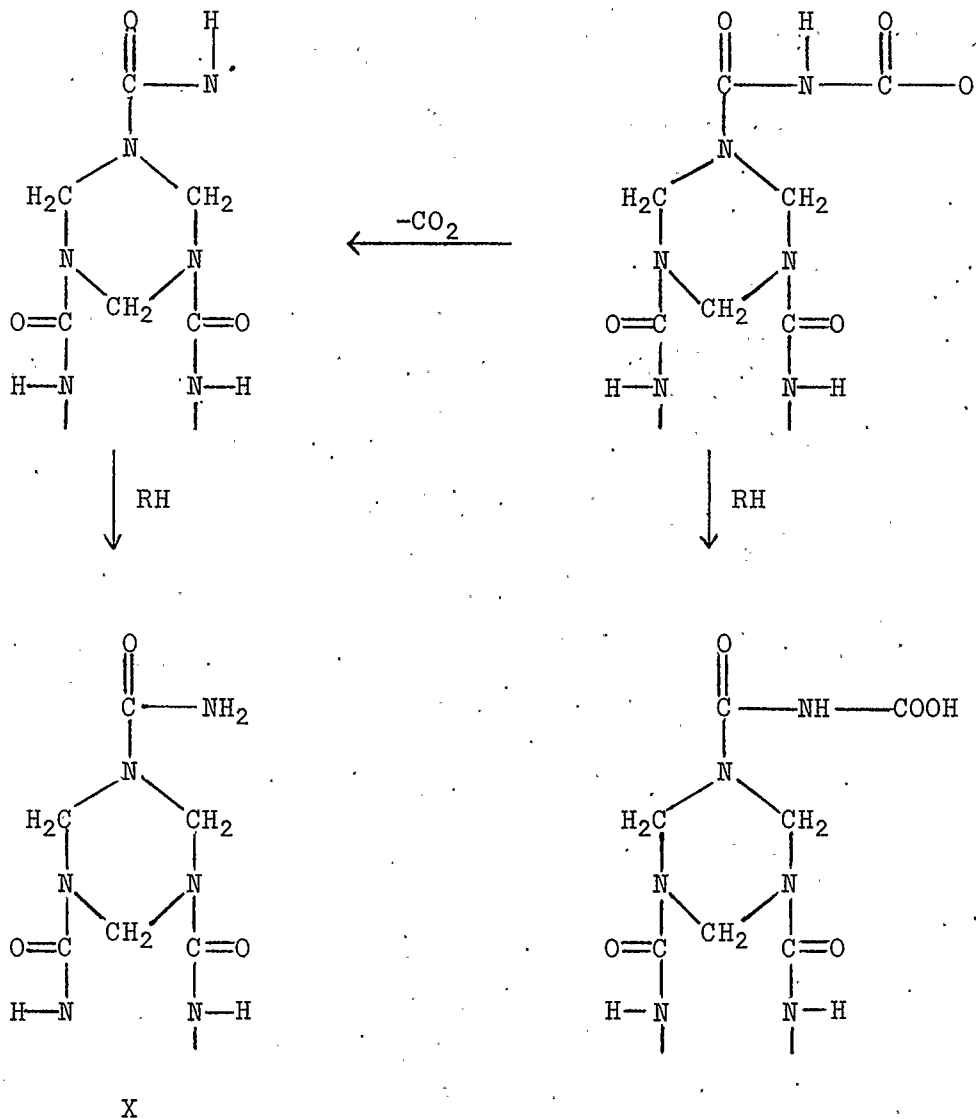


According to Sharkey and Mochel the hydroperoxide formed (IX) will be transformed finally into a hydroxy-alkylamide group, which may be decomposed as follows:



The aldehyde formed. (VII) can be decomposed as follows with the evolution of CO₂, CO.





This hypothesis provides a possible explanation of most of the experimental facts found in this work. The formation of the primary amide group provides an explanation for the over 50% by weight chlorine found in the prechlorinated resins.

The acid grouping shown in compound IX, explains the amount of NaOH consumed during the chlorination process.

The evolution of CO_2 and CO were also explained according to this mechanism. It will be noted however, that no explanation

was given for the production of nitrogen. This was not an oversight. No satisfactory explanation was devised for this product of self-oxidation.

3.6 Conclusion:

From the above study of the stability of chlorinated UMF resins and similar formulations, it can be concluded that all of these chlorinated resins when immersed in water give off gases i.e. are subject to slower or faster self-oxidation.

It was found that resin 53-1 is more stable than Dewar resin. Also, the stability of the resins varies from one resin to another depending on their structure i.e. the availability of the easily oxidizable groups.

The multiple chlorination process was found to be one of the more important easily available processes to improve the stability of the chlorinated resins. The self-oxidation could also be reduced by raising the temperature during the chlorination process.

A hypothesis for a mechanism to explain the self-oxidation process is proposed. It is suggested that this is a free radical mechanism depending on the availability of oxygen-carriers. Arguing by analogy and on the basis of our own experimental results, it was concluded that the amide molecule is primarily attacked at the $-CH_2$ group next to the $-NH$ group. This hypothesis provides an explanation both for the gas evolution, the amount of NaOH consumed during chlorination and the over 50% by weight chlorine content found in the resins subjected to the pre-chlorination process.

Chapter Four

EXPERIMENTAL

4.1 Preparation of Materials

4.1.1 Purity of water:

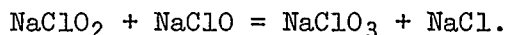
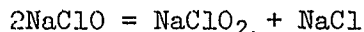
An impurity in water subject to oxidation by chlorine will introduce a serious error since an equivalent amount of Cl^* will disappear and create a like amount of HCl . The necessary purity of water was achieved by the redistillation of doubly distilled water attained from a Corning system.

4.1.2 Preparation of sodium hypochlorite solution:

A solution of sodium hypochlorite was prepared according to equation (2.5)



For a typical experiment described above in Section 2.3 the sodium hydroxide solution was prepared by dissolving 4 g NaOH in 500 cc doubled distilled water. Side-reactions were reduced by precooling the NaOH solution using ice-water surrounding the three necked flask which contained the above solution. Reaction (2.5) was allowed to take place by slowly bubbling chlorine gas through the NaOH solution while the mixture was constantly stirred. The chlorine gas was bubbled until the desired value of the available chlorine content was achieved (0.122 M), as checked by iodometric analysis. Cooling was necessary to prevent the formation of ClO_3^- according to the equations:



The formation of ClO_3^- depends on the concentration of NaClO , and also, on the temperature. Since we are dealing with a low concentration of HOCl (0.122 M), the tendency to form ClO_3^- ions was reduced and if any ClO_3^- was formed at higher temperature (40°C), it was found to be less than 0.1%..

4.2 Description of Apparatus:

4.2.1 Apparatus for chlorinating and measuring the self-oxidation of the resin:

The apparatus used for chlorinating the resin and measuring the rate of oxidation consists of the following:

- (a) A 1000 ml four necked round bottom flask with stirrer shaft was used as a reaction container.
- (b) Stirring rack, stirring motor and plate form.
- (c) A 10 ml precision syringe.
- (d) Delivery tube with stop-cork for delivering standard NaOH solution to the reaction container.
- (e) A KNO_3 bridge consisting of a standard 3-way glass tube with fritted disks.
- (f) A pH meter (Fisher Model 320), with a glass and calomel electrodes.
- (g) An automatic timer and printer.

The pH-stat was assembled using a 10 ml precision syringe which was designed by Robertson et al⁶³. The reproducibility of the syringe was accurate to better than 0.01 ml. Using this syringe, the number of counts recorded is converted to millilitres (ml/counts = 0.753×10^{-3}).

The syringe was modified with an electrical contact Veeder Root counter which was connected to a Hewlett Packard model 56A Digital Recorder. A clock using a similar counter driven by a Synchronour motor plus a memory unit for $1/10$ minute was also connected to the same recorder. Print out and control of the motor drive on the syringe was obtained by an electrical circuit. A block diagram for the system used is shown in Fig. 4.1.

The pH meter converts the potential difference between the glass and reference electrodes to a current output at the recorder terminals, and provides an accurate indication of pH.

The output at the recorder terminals is ± 1 milliamperes for full scale deflection of the meter. This corresponds to ± 7 pH units on a scale centered at pH 7 or ± 0.7 pH on expanded mode. The output current may be used directly or converted to a voltage by connecting a resistor of up to 50 ohms across the recorder terminals. (Fisher instruction manual No. 19750).

The operational amplifier operates as a current to voltage converter. This configuration was chosen over that of a voltage amplifier because it offers greater signal to noise ratio and stability.

The output of the amplifier is ± 10 volts for an input of ± 1 ma. High frequency response is limited to 34 hertz to reduce

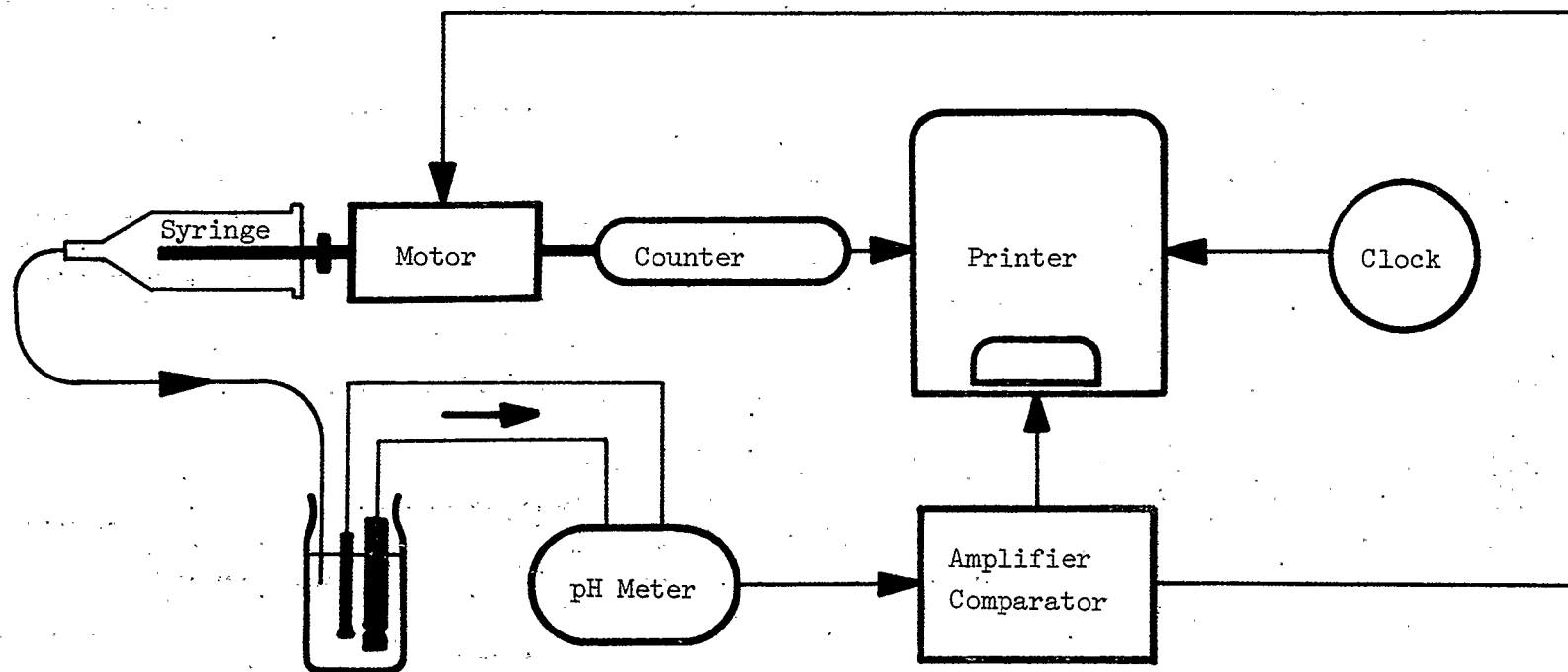


Fig. 4.1 Block diagram for the system used for the chlorination process.

high frequency noise and 60 HZ. power line interference.

The comparator accepts the ± 10 volt output from the operational amplifier, a set-point input, and a window-width input. The set-point and window-width may be carried independently over the full ± 10 volt (± 7 pH) range of the input from the operational amplifier. In this case the set-point and window-width were restricted to 5 volts (3.5 pH units) to enhance resolution.

There are three digital voltage outputs HIGH, GO, and LOW. When the input signal is inside the "window" the GO output rises to +12 volts. If the input signal drops below the window value the LOW output will rise to +12 volts and the GO output will fall to zero. When the value of the input signal exceeds the window level the HIGH output goes to +12 volts. The three outputs are mutually exclusive. Fig. 4.2 shows the comparator output.

The HIGH and LOW outputs are interfaced to a bistable integrated circuit which drives a pair of relays. One relay is used to enable the syringe motor while the other activates the printer which records time and volume.

In summary the system was so arranged that on reaching the lower limiting pH (say 0.1 pH unit below the standard) the syringe motor was activated and slowly pumped base into the reaction system until the standard⁶⁴ was reached. At this point the motor turned off. There was usually a slight "overshoot" which can be adjusted automatically by the machine until the standard value was reached again. When the machine prints out volume and corresponding time it repeats the cycle.

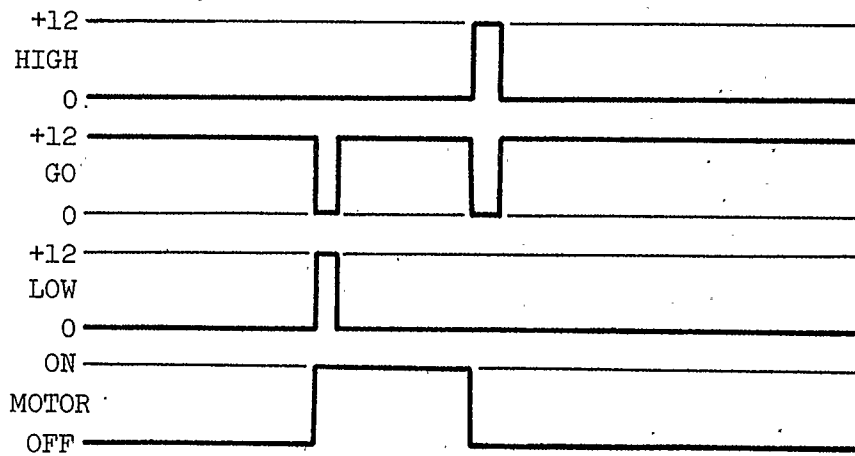
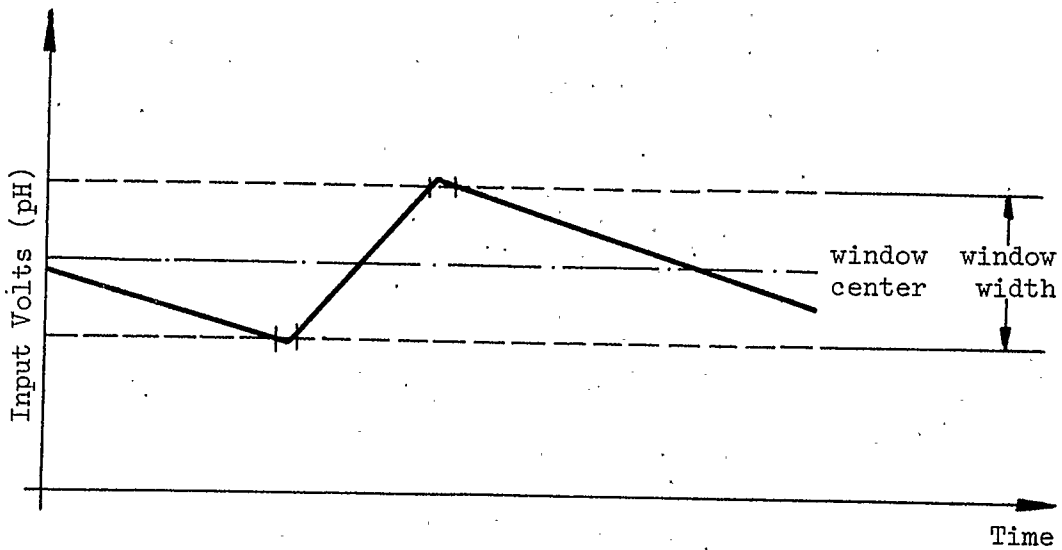


Fig. 4.2 Comparator output.

4.2.2 Apparatus for self-oxidation test:

Since a large number of samples have to be examined over a period of two weeks or more, a simple testing system was developed for measuring the stability of chlorinated resins. This system depends on measuring the gases evolved from a standard sample of chlorinated resins. The idea behind this apparatus was to gain a relative measure of stability rather than an absolute measure. This system consists of a large number of test tubes approximately 13 x 100 mm which were inverted in a water trough. A 1.0 g sample of the chlorinated polymer was weighed into the test tube, while a 1¹/₄" square piece of polypropylene cloth, mesh size \approx 80 was wrapped over the open end of the tube and fastened with a small rubber band. Double distilled water was poured into the tube, while tube and contents were agitated to remove gas bubbles from the sample. The inverted tube was placed in the trough of water and fastened to one side by a rubber band. For convenience in measurement all the inverted tubes initially should have no gases at all.

The amount of gases were measured in mm and as a check on the reproducibility of results, duplicate samples of each resin were tested.

Constant temperature bath:

The reactions were run in a constant temperature bath with control to $\pm 0.01^{\circ}\text{C}$ or better. The temperature was measured with a platinum resistance thermometer.

4.3 Analyses:

4.3.1 Analysis of positive chlorine:

The iodometric method⁶⁴ was used for analysis of positive chlorine both in solution and on the chlorine exchange resins since the positive chlorine is present in a concentration above 10 ppm.

The method for analysis of chlorine on the resin involving contacting the resin with an excess of KI dissolved in a strong acetic-acid-sodium acetate buffer (pH approximately 4.5). This resulted in iodine liberation according to the equation



The I₂ was then leached out of the resin by an excess of standardized sodium thiosulfate solution, followed by a back titration of the excess thiosulfate using standard iodine solution. Completion of the leaching process was observed by the disappearance of the red-brown iodine colour from the resin (15 to 45 minutes).

The strong buffer solution must be sufficiently acidic to supply sufficient H⁺ ions for I₂ liberations and yet prevent side reactions of thiosulfate.

The analysis of positive chlorine on the resin was speeded up by crushing the resin in an agate vial with a ball made of either agate or hardened steel. The vial and contents are agitated in a high-speed mechanical mill, such as the Glen Creston Analytical Mixer Mill. The grinding time is usually 1¹/₂ to 2 minutes which should be long enough to form a very fine powder and yet not allow

any appreciable loss of chlorine.

At least two samples of the resin were analyzed for the apparent concentration of positive chlorine in the resin. The volume of thiosulfate is related to the volume of I₂ solution according to the following equation³³

$$V_{I_2} = V_{thio} \times \frac{N_{thio}}{NI_2} + V_{correction}$$

where

V_{I_2} = total volume of I₂ solution.

V_{thio} = volume of thiosulfate solution.

$V_{correction}$ = titration error expressed as volume of I₂ solution.

If V_{I_2} is plotted against V_{thio} the slope is N_{thio}/NI_2 and the intercept is $V_{correction}$. A plot of these values was found to give a straight line with very little deviation from linearity. Since the values for $V_{correction}$ were found to be less than 0.1 ml of I₂ solution and in most cases were close to 0.05 ml, therefore this $V_{correction}$ was neglected in our analysis. The error in the standardization of sodium thiosulfate (0.1 and 0.01 N) against potassium dichromate was found to have accuracy of ± 1%. This assumed that the potassium dichromate was as pure as specified.

4.3.2 Gas Analysis:

The gases evolved from the chlorinated resins were analyzed

using the mass spectrometer, VARIAN MAT CH5. The gas sample was collected by means of a gas syringe from the inverted tube which trapped the gases under water. The gas sample container was evacuated first, then by means of a small-bore tube, some of the gas sample was drawn from the inverted collector tube to displace the air in the small bore-tube and thereby nullify the error due to that air. The sample container was reevacuated and the background spectrum was obtained. More gas sample was drawn in and this was supplied to the mass spectrometer and the actual analysis was recorded.

The possibility that more than one ion species were in the spectra corresponding to $m/e = 28$ was confirmed by isolating this mass using a high-resolution. It was found that this mass contains mainly N_2 , and small amount of CO. The other major component was CO_2 .

Chapter Five

CONCLUSION

This work deals with the practical problem of stability of chlorinated UMF resins. These resins are insoluble, therefore one can only speculate about the structure. This was accepted as a necessary restriction and the practical question was studied in spite of this unknown.

The effect of changing various factors which influence the chlorination of UMF resins and eight different formulations were studied. The tests applied in evaluating the effect of this change were directed primarily to stability i.e. resistance of the chlorinated resin to self-oxidation. The factors influencing chlorination under investigation were pH, temperature, chlorine concentration, grain sizes, the resin/HOCl ratio, the effect of added chlorate, chloride, and chlorite in the chlorinating medium.

It was found that the variation of pH in the range (4-6) has but a slight effect on the total chlorine absorbed by the resin and the amount of resin oxidized during the chlorination process to give acid.

In the investigation of the effect of the ratio of initial chlorine concentration to resin, it was found that the rate of chlorination and of oxidation is related to the initial chlorine concentration. Higher concentrations of HOCl appear to accelerate undesirable oxidation of the easily oxidizable group in the resin. Therefore, a lower concentration is better for chlorination although a longer reaction time will be required to achieve maximum loading.

From a study of the effect of grain sizes and resin amounts, it was found that the rate of absorption and liberation of available chlorine are governed by diffusion control rather than by reaction control alone particularly for larger grain-sizes. Since the resin has a macro-reticular structure, this was to be expected.

While the effect of added chlorite ions to the chlorinating medium produced a chlorinated resin with slightly higher weight percent active chlorine, this did not seem to introduce any important change in the chlorine content or in the amount of oxidation during chlorination. The introduction of Cl^- and ClO_3^- ions to the chlorinating solution has no effect on the chlorine absorption except that there was a greater production of gases in the case of added chloride ion.

Raising the temperature of chlorination was found to increase the total degree of oxidation and the resulting chlorinated resins showed a significant improvement in stability provided the HOCl/resin ratio was low.

Changes in polymer composition produce significant differences in the chlorinated resin both with respect to oxidation in the chlorination process and in stability under actual conditions of use.

The rate of oxidation of the resin was studied; it was found that the rate follows a pseudo first-order kinetics and increases by raising the temperature. This rate of oxidation was shown to be different for different formulations of the UMF resins.

The stability to self-oxidation of such chlorinated resins resulting from changing the above noted factors in the chlorination process were investigated. All the resins under consideration were

found to be subject to slower or faster self-oxidation. It was found that the 53-1 resin is relatively more stable than Dewar resin. It was concluded that the stability varied from one resin to another depending on the initial structure of the resin and this could be improved by removal of the easily oxidizable groups. This improvement can be achieved to a remarkable degree by following the multiple chlorination process; also by raising the temperature during the chlorination period.

A hypothesis for explaining the mechanism of self-oxidation process was proposed. This is a free radical mechanism in which the amide molecule is primarily attacked at the $> \text{CH}_2-$ group next to the $> \text{NH}-$ group. This hypothesis provides a good explanation both for the gas evolution, the amount of NaOH consumed during chlorination and the over 50% by weight chlorine content found in the resins subjected to the pre-chlorination process.

REFERENCES

1. G. M. Fair, J. C. Morris, S. L. Chang, I. Weil, and P. Robert, J. Am. Water Works Assoc., 40, 1051 (Oct. 1948).
2. G. A. Johnson, J. Pub. Health, 1, (1911).
3. J. L. Leal, Proc. Am. Water Works Assoc., 100 (1909).
4. C. R. Darnall, Am. J. Pub. Health, 1, 783 (1911).
5. H. A. Faber, Water and Sewage Works, 98, 455, (Nov. 1952).
6. N. J. Howard, The American City, 791 (June 1927).
7. A. E. Griffen, J. New England Water Works Assn., 58, 322 (1944).
8. American Water Works Association, Inc., "*Water Quality and Treatment*", Ed. 2, Lancaster, Lancaster Press Inc., (1955).
9. A. Wolman, W. Donaldson and L. H. Enslow, J. Am. Water Works Assoc., 22 (9), 1161 (Sept. 1930).
10. J. W. McAmis, J. Am. Water Works Assoc., 17, 341 (March 1927).
11. J. Race, "*Chlorination of Water*", Ed. 1, New York, John Wiley & Sons Inc. (1918).
12. D. E. Green, and P. K. Stumpf, J. Am. Water Works Assoc., 38, 1301 (1944).
13. L. H. Enslow, J. Am. Water Works Assoc., 20 (6), 819 (Dec. 1928).
14. H. A. Faber, J. Am. Water Works Assoc., 39 (3), 200 (March, 1947).
15. A. E. Griffin, J. Am. Water Works Assoc., 31, 2121 (1939).
16. M. Wayman, H. Salamat, and E. J. Dewar, C. J. Chem. Eng., 46, 282 (1968).
17. R. E. Corbett, W. S. Matcalf, and F. G. Soper, J. Chem. Soc., 1927 (1953).
18. C. R. Edmond and F. G. Soper, J. Chem. Soc., 2942 (1949).

19. F. B. Hurst and F. G. Soper, J. Chem. Soc., 107 (1949).
20. R. P. Mauger and F. G. Soper, J. Chem. Soc., 71 (1946).
21. F. G. Soper, J. Chem. Soc., 125, 1899-1910 (1924).
22. F. G. Soper, J. Chem. Soc., 127, 98-102 (1925).
23. M. Wayman and E.W.C.W. Thomm, C. J. Chem., 47, 2561-2567 (1969).
24. E.W.C.W. Thomm and M. Wayman, C. J. Chem., 47, 3289-3297 (1969).
25. M. Wayman and E.W.C.W. Thomm, C. J. Chem., 48, 495-466 (1970).
26. Kirk and Othmer, *Encyclopedia of Chemical Technology*, Interscience, N.Y., (1964).
27. B. N. Israel, "*Hydrolysis of some Organohalogenating Agents*", Ph.D. Thesis, Univ. Wisconsin (1962).
28. H. D. Dakin, J. B. Cohen, M. Daufresne, and J. Kenyon, Proc. Royal Soc. London ser. B, 232-251 (1916).
29. F.J.C. Weber, U.S. Pat. 2, 898, 264 (Aug. 1959), (to Colgate-Palmolive Co.).
30. K. Ziegler, Ann. Chim., 551, 80-119 (1942).
31. W. Lorenz, Brit. Pat. 824, 199 (Nov. 1959), (to Purex Co.).
32. I. E. Muskat and A. G. Chenicek, U.S. Pats. 2, 184, 883; 2, 184, 886; 2, 184, 888 (Dec. 1939), (To Pittsburgh Plate Glass Co.).
33. E. J. Dewar, "*Study of the Properties of Chlorine Exchange Resins*", Ph.D. Thesis, Univ. of Toronto (1969).
34. W. Blakey, Chem. Ind., 1349 (1964).
35. H. John, Brit. Pat. 151, 016 (1918).
36. C. S. Marvel, J. R. Elliott, F. E. Boettner, and H. Yuska, Am. Chem. Soc., 68, 1681-6 (1946).

37. R. W. Lenz, *Organic Chemistry of Synthetic High Polymers*, New York, John Wiley & Sons Inc. (1967).
38. B. Bann and S. A. Miller, *Chem. Rev.*, 58, 146 (1958).
39. P.B.D. De La Mare, J. T. Harvey, M. Hassan, and S. Verma, *J. Chem. Soc.*, 2756 (1958).
40. P.B.D. De La Mare, I. C. Hilton, and C. A. Vernon, *J. Chem. Soc.*, 4039 (1960).
41. C. G. Swain and R. C. Delanson, *J. Am. Chem. Soc.*, 49 (9), 3195-3200 (1972).
42. M. Anbar and I. Dostrovsky, *J. Chem. Soc.*, 1094 (1954).
43. J. March, *Advanced Organic Chemistry, Reactions, Mechanism, and Structures*, McGraw-Hill Inc., 1970.
44. J. S. Scone, *Chlorine, its Manufacture, Properties and Uses* (ACS monograph Series 154) Reinhold, London, (1962).
45. D. P. Horning and R. E. Robertson, unpublished work, Univ. of Calgary (1972).
46. R. E. Connick and Y. T. Chia, *J. Am. Chem. Soc.*, 1280 (1959).
47. I. E. Flis and M. K. Bynyaeva, *Zhur. Prikladn. Khim.*, 30, 337 (1957).
48. I. E. Flis, K. D. Dobryshin, and I. I. Bloshtein. *Tr. Leninger. Tekhnol. Inst. Tsellyulozn-Bumazhn. prom. No. 16*, 31-7 (1965).
49. I. E. Flis, K. P. Mishchenko, and K. Yu. Salni, *Zh. Prikl. Khim.* 35, 667-9 (1962).
50. I. E. Flis, *Zh. Prikl. Khim.*, 29, 633-45 (1956).
51. G. L. Cunningham and B. J. Losch, U.S. Patent 2, 043, 284 (June 9, 1936) (To Methieson alkali works).
52. F. Forster and P. Z. Dolch, *Electro Chem.*, 23, 137 (1917).

53. D. Swern, *in Autoxidation and Antioxidants*, Vol. 1, W.O. Lundberg, Interscience, New York (1961).
54. W. H. Sharkey and W. E. Mochel, *J. Am. Chem. Soc.*, 81, 3000 (1959).
55. E. M. Boasson, B. Kamerbeck, A. Algera, and G. H. Kroes, *Rec. Trav. Chim.*, 81, 624 (1962).
56. G. H. Kroes, *Rec. Trav. Chim.*, 82, 979 (1963).
57. E. Milolajewski, J. Swallow, and M. Webb, *J. Appl. Polymer Sci.*, 8, 2067 (1964).
58. I. E. Flis, T. A. Tumanova, and T. T. Grigor, translation from *Zhurnal Prikladnoi Khimii*, 41 (10), 2245-2251 (1968).
59. V. Hanal and J. M. Smith, *Ind. Eng. Chem. process Des. Develop.*, 10, 515-23 (1971).
60. I. E. Flis, K. P. Mishchenko, and N. V. Pakhomova. *Zhur. Neorg. Khim.* 3, 1781-4 (1958).
61. K. U. Ingold, *Chemical review*, 61, (1961).
62. L. Reich and S. S. Stivala, *Autoxidation of Hydrocarbons and Polyolefins*, Marcel Dekker, Inc., New York (1969).
63. S. Martin, R. E. Robertson, and G. C. Benson, *Sci. Inst.*, 41, 237-238 (1964).
64. American Public Health Association, Inc., *Standard Methods of Examination of Water and Waste Water*, Am. Pub. Health Ass., N.Y., 11th ed., (1960).