DEGRADATION AND STABILIZATION OF VINYLCHLORIDE BASED POLYMERS

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by

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Acknowledgements

We'd like to begin our acknowledgement with the quotation by Charles Maurice de Talleyrand-Périgord, a famous French statesman and diplomat who said that "coffee should be black as night, sweet as sin, hot as love and strong as curse". We think that the persons who contributed to publishing the present monograph, and their activities can be characterized by the perfection of this refreshing drink.

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F. M. Dostoevsky, a Russian writer, said once that if the mankind was to face the Judgment Day, Miguel de Cervantes's novel "Don Quixote" will be a sufficient ground for the people to justify themselves. As compared with this book our monograph is surely only a very small contribution. However, we cherish the hope that if the topic theme of the Judgment Day covers ageing and stabilization of chlorine-containing polymers, we may expect to obtain mercy.

Preface to the Russian Edition

This book written by K. S. Minsker, S. V. Kolesov and G. E. Zaikov now offered to the reader deals with a very urgent topic—the theoretical and practical aspects of degradation, stabilization and prediction of useful lifetimes of poly(vinyl chloride) and other vinyl chloride-based polymers. The authors have been able to spotlight the reasons of the poor stability of VC homo- and copolymers, develop a quantitative kinetic approach to degradation of these polymers and work out a general theory of their degradation and stabilization. An important aspect of the book is that a quantitative approach to prediction of the durability of polymers and articles made of them under various service and storage conditions has been proposed for the first time.

Recently the INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY organized a special commission charged with the task of finding out the reasons behind the poor stability of PVC, revealing the structural defects of PVC chains. The authors of this book, while not being members of this commission, have been carrying out an independent investigation of this problem and have been able to identify the macromolecular defects and estimate their reactivity.

I believe that the new book packed with fresh information on the subject, will meet readers' interest.

N. M. Emanuel,
Member of the USSR Academy of Sciences

Introduction to the English Edition

"Science is precisely what *cannot be*; what *can be* is the "scientific and technical progress"".

—E. L. Andronikoshvili

We have chosen this epigraph because it epitomizes the somewhat controversial nature of the subject matter of this book. The object of this work has been to find the cause of the low stability of poly(vinyl chloride) and other polymers containing the VC group in their chains. It has been found that there are some groups which appear in the polymer chain for one reason or another which, once generated, deteriorate the stability of polymers to a level much below that which one would expect on the basis of the ideal chemical formula abbreviated as PVC.

This book contains the first-ever quantitative treatment of the experimental data on the mechanism and kinetics of the degradation of the polymer chain of poly(vinyl chloride) and VC-based copolymers. The problems of chemical and physical ageing of vinyl chloride copolymers and the prediction of service lifetimes of the products on the basis of these have been highlighted with much detail. Particular attention has been paid to the carbonyl-allyl groups accumulated in such polymers and actually responsible for their low stability. The role of these groups is not currently realized by all investigators in the field. For example, in one of the most recent publications on the subject ("Degradation and Stabilisation of PVC", ed. by E. D. Owen, London, Elsevier Applied Science Publishers, 1984) carbonyl-allyls are simply not considered as a potential cause of PVC instability, all attention being centered on the previously known and more "traditional" defects. These are many historical examples of cases in which facts were stubbornly refuted and which later found their way to recognition. For example, back in 1895 the world-famous British physicist and mathematician Lord Kelwin (William Thomson) contended that "it is impossible to fly on an apparatus which is heavier than air"; two years later he claimed that "the wireless has no future", another three years passed and he announced in 1900 that "X-rays are no more than a joke".

We hope that the abundant evidence contained in the book will convince the reader that the defects we have mentioned are no joke but are altogether

real and have to be considered in any attempt to improve the stability of PVC-based polymers. Many researchers in the field will probably be reluctant to accept the conclusions reached in this book and it remains for us to hope that time will remedy the situation. If, for all that, we fail to persuade some readers we will cherish the hope that the wealth of other valuable data in the book will be of interest to the reader. Primarily it is the kinetic approach which is a methodological instrument for the study of chemical processes with a view to controlling them.

Borrowing the simile from the American writer O'Henry, the volume contains information both about "kings and cabbages" of PVC science up to 1984 inclusive. But we have also taken heed of what great Voltaire said: "...the secret of being boresome and annoying is to seek to tell all there is to say...".

We have been looking for a simple theory, mindful of Newton's words that "...nature is simple and does not abound in superfluous causes...".

The book is addressed to a wide circle of chemists with interest in high molecular compounds and chemical kinetics.

K. S. Minsker
S. V. Kolesov
G. E. Zaikov

Introduction to the Russian Edition

Today the worldwide production of polymers amounts to 100 million tons and by the year 2000 the figure is expected to double. If the data are converted to the volumetric instead of weight scale the polymer output will be expressed by a figure which will be of about the same order of magnitude as the output of, say, iron, steel or rolled products. Considering such a huge scale of production, the extension of the service life of polymer products is an extremely important economic problem which is equivalent in importance to the increase of the industrial output and improvement of product quality. This is in fact one of the most urgent problems currently faced by research and practical chemists working in the field of high-molecular compounds. The second important problem is to be able to accurately predict the life expectancy of polymer products under various service and storage conditions. Underestimation of the service lifetime of plastic components will result in their premature replacement which is economically unacceptable. Overestimation may also lead to dramatic consequences because a unit or part may fail well before the expected time and cause sudden breakdown of a critical piece of equipment.

Yet there are cases where ageing is desirable. This is so, for example, when degradation is used as a means of modifying polymer properties (e.g., to impart roughness to the surface, generation of micropores, etc.).

Finally, the search for ways to improve stability and the relationship between stability and other polymer properties (physical, mechanical, electrical, etc.) are gaining importance in the regeneration of used plastics. Over the years the problem can only be expected to gain in urgency as plastics output increases and the environment protection laws become more severe.

To be able to tackle these four problems successfully one must know the kinetic laws and mechanisms which control PVC degradation and have at ones disposal rigorous theoretical principles of stabilization of particular polymer types used under specific environmental conditions.

Poly(vinyl chloride) and its copolymers are currently produced in greater quantities than any other single polymer. The reason is that they have found extremely varied applications in different branches of industry, agriculture and, of course, household applications. Today the annual output of PVC is 10 million tons. USA alone produce 3 million tons and the Western Europe

about 4 million tons annually. Investigation of degradation and a search of the ways and means for stabilization of this important class of plastics is in fact what this book is all about.

K. S. Minsker
S. V. Kolesov
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Introduction

Perhaps the most conspicuous feature of the technical progress of XX-th century has been deep and wide penetration of polymeric materials into all fields of human endeavor. This has been made possible primarily by the ready availability and cheapness of the raw materials, the simplicity of the manufacturing process, processability into articles of complex shape by means of highly productive and simple technological steps, and the possibility of imparting to polymers practically any conceivable set of desired properties (specific weight, chemical stability, strength, electric parameters, etc.). From "substitutes" which plastics were back in 30's and 40's, polymers have now become indispensable materials. At the same time, their more than half a century of use has revealed some shortcomings common to all of these new materials. Probably the most important of these is the tendency of most synthetic polymers to what is called "ageing".

Polymer ageing is in fact a series of chemical and physical transformations occurring in the polymer during service, processing or storage which causes deterioration in valuable properties [1].

Many factors are responsible for polymer ageing, including heat and mechanical loads, chemically active liquid or gaseous media, UV radiation, ionizing radiation, biological agents and many others. These factors, active either separately or together, depending on the chemical structure of the polymer, cause complex parallel-sequential processes including cracking (degradation), depolymerization, cross-linking, conversions of the surrounding groups, oxidation, etc.

It is these reactions which cause considerable and often quite rapid deterioration of polymer properties, sharply leading to a sharp decrease in their useful life.

It should be remembered that a real polymer is, as a rule, a complex system including, apart from the main component (a high-molecular compound), various additives and impurities (softeners, fillers, pigments, stabilizers, metal deactivators and their salts, flame retardants, pesticides, catalyst traces, traces of initiators, protective colloids, emulsifiers, etc.). Therefore, the investigation of such a phenomenon as ageing must necessarily cover a wide range of problems in the fields of chemistry and physics of radical, ionic and molecular

reactions in a multicomponent system prepared from standard-grade individual polymers.

A multitude of chemical reactions usually take place in a real system, depending primarily on the stability of the base polymer which, in turn, is determined chiefly by the chemical nature of the macromolecules and then by the concentration and type of structural irregularities present, the physical structure of the material, the presence of additives and impurities and external physical effects.

At present the world's output of various plastic materials amounts to over 50 million tons annually, and their protection from all forms of ageing, i.e. stabilization of polymer properties, is therefore an extremely important economic problem.

Yet, the importance of the problem of polymer stabilization is not solely an economic consideration. In many cases a long service life is a technical prerequisite. Further, many polymer products cannot be processed into finished articles at all, unless previously stabilized. On the first hand they include vinyl chloride-based homo- and copolymers, the truly universal compounds included as basic components in many thousands of special- and general-purpose compositions and products, both plasticized (soft and semi-soft) and nonplasticized (rigid, solid).

Vinyl chloride-based plastics are produced in enormous quantities. Currently the annual production of PVC is ca. 11 million tons and the production capacities amount to 17 million tons per year [2]. PVC is manufactured in more than 40 countries, about 70% of the whole output being produced in the USA, Japan, West Germany, Great Britain, Italy and the USSR.

There are no conceivable reasons to expect a sharp reduction in polymer production in the future [3]. The world's annual output of poly(vinyl chloride) is expected to increase up to 31.1 million tons in 1990 [4].

It may be interesting to note that vinyl chloride-based plastics production which was initially first and then second among other plastics, has gone through several stages of development.

In 1970 and 1971, following a fairly long period of prosperity, the vinyl chloride polymer industry suffered a depression due primarily to a changeover to a different basic raw material (from carbide acetylene to ethylene).

In 1972 and 1973 the situation was more stable but in most countries the rate of growth of production was not high.

In 1974/5 the production and usage of polymers sharply declined which was primarily associated with the oil crisis. Also, during this period questions of the alleged health hazard of vinyl chloride-based polymer products were widely publicized. The equipment used for the production and processing of plastics underwent major renovation in the meantime.

But in 1976 a tendency to a more brisk growth of PVC production finally took shape. In 1980, the growth of production and use of polymers was 10 to 12 wt.%.

The past decade signifies an important stage during which new tendencies have taken shape and established themselves to such an extent that they will presumably control the prospective development of PVC production during the forthcoming 10 to 15 years.

Three PVC production processes now dominate the scene, viz. emulsion, suspension and bulk polymerization. In 1981 79% of total production was by suspension polymerization, 10% by emulsion polymerization, 9% by bulk polymerization and 2% (some certain VC copolymers) by polymerization in solution [5]. The importance of the emulsion process in total PVC output will in the future depend mainly on the quantity of polymer processed through the plastisol stage and also used in manufacturing of commercial latexes, for example, for impregnation of paper and fabrics, production of nonwoven fabrics, in polymer-cement compositions, etc. It is much more difficult to foresee the evolution of the ratio of PVC grades produced by suspension and bulk polymerization, although the tendency which seems to be revealed itself in recent years has apparently been in favor of suspension.

The steady increase of the production and use of vinyl chloride polymers is due to their serious advantages over the other competitive synthetic resins and plastics. These advantages include, in particular,

a) the content of more than 50 wt. % of the inorganic component (chlorine);

b) cheapness due to the low net cost of production offered by the use of petrochemical raw material in the monomer production and high perfection of the manufacturing processes. However, considering the current rate of growth of oil prices one might expect in the conceivable future a reversed tendency to return to nonpetrochemical raw materials;

c) superior physico-mechanical properties and unplasticized chemical stability;

d) large assortment of materials and products possessing a wide range of specifications;

e) steady improvement of the quality of the resin, softening agents and other secondary ingredients;

f) constant improvement of processing technology.

From the above it follows unambiguously that the research into both the intrinsic stability of vinyl chloride polymers and their degradation and stabilization is an urgent problem of worldwide interest.

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