NUCLEAR RESEARCH EMULSIONS

A TREATISE IN TWO VOLUMES

I. Techniques and Theory
II. Particle Behavior and Emulsion Applications

NUCLEAR RESEARCH EMULSIONS

I. Techniques and Theory

PURE AND APPLIED PHYSICS

A SERIES OF MONOGRAPHS AND TEXTBOOKS

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NUCLEAR RESEARCH EMULSIONS

Walter H. Barkas
University of California
Berkeley, California

I.

Techniques and Theory

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This book is affectionately inscribed to the score of able young men who have worked with me on their Ph.D research.

PREFACE

This two-part work is on a subject which has grown to maturity in the past fifteen years. While its ultimate development certainly has not been reached, some stability is now being experienced, and a comprehensive work can be attempted.

These volumes grew out of needs felt during a period of years for a source of answers to questions asked by students and others. The work was first started as a graduate seminar which the writer gave at the University of California in Los Angeles during the spring of 1954. It was accelerated during the summer of 1957 with help from both the National Science Foundation and the U. S. Atomic Energy Commission.

Much lore, to be distinguished from something resembling witchcraft that occasionally has been encountered, exists in connection with the use of nuclear research emulsions. Information of this sort, however, is scattered throughout the scientific literature, or has been passed on only orally. It thus has been largely inaccessible to a busy worker who wishes to use this instrument, but who has not had years experience with the medium.

Part I of this work brings to the reader information of a practical nature that world sources and the writer's experience affords. On many topics it is therefore not more or less than a homely "cookbook." Most scientific subjects, as well as the technical ones, are first treated in a simple, elementary way. Those that lend themselves to deeper analysis are subsequently discussed from this standpoint. Many subjects will be found to be presented quantitatively for the first time in this volume. A majority of the sections contain new, previously unpublished material. An earnest effort has been made to present more than mere qualitative information and to avoid ambiguity. Tables or graphs are presented for every process on which data could be obtained. Often a single entry has required that the author make measurements or long calculations to find it. A definite bias exists toward regarding emulsion as a *quantitative* instrument.

Throughout, examples have been freely drawn from the literature. To be completely exhaustive is essayed, however, only on very important topics and in areas where a shortage of information exists. In an attempt to make this work useful rather than merely encyclopedic, an editorial responsibility has been assumed. It has been considered unnecessary to quote incorrect results, or *all* sources; just the references believed to be the most reliable are included. When data are limited, what is available is cited unless it is known to be wrong.

The work is written for advanced students in the physical sciences, earth sciences, and bio-sciences. Another group who may find it useful is composed of active research workers who have been employing other techniques, but realize that for a particular task, emulsion has valuable attributes. A third is comprised of people, even those quite experienced in the field, who want a ready reference to the whole technology and science of nuclear research emulsions. Finally, this book is directed to anyone who wishes to broaden his scope by mastering another instrument. It can be studied profitably by amateur scientists of any age as well as by professionals.

Part I begins by indicating the areas in which emulsion is usefully employed. The first chapter is completed by compiling technical information and sources of supply of the present emulsion types. The second chapter reviews the phenomena of silver halide sensitivity, current research in this field, and especially the processes of importance for the materialization of charged-particle tracks. Chapter 3 is devoted to the physical and chemical constitution of emulsion, and contains much information unavailable anywhere else. Chapters 4 and 5 describe the methods for handling and processing emulsion in its various forms. Chapter 6 is devoted to the mechanical and optical properties of the processed emulsion. New information is introduced on the types and consequences of distortion in processed emulsion. Chapter 7 is given over to microscopy and photomicroscopy of emulsion tracks, recommended equipment, scanning procedures, automatic equipment, and some mathematical analysis of practical situations. Chapter 8 is a rather extensive treatment of an essential topic. It analyzes particle scattering in matter of which emulsion is a particular, and here an important, example. The techniques and equipment for measuring particle scattering are elaborated. In Chapter 9 the linear and transverse track structure is analyzed. The relationship of the particle velocity and charge to the track featurés are developed. The author's theory of the linear track structure is presented. Part I ends with a chapter on particle range and range straggling. Again a detailed treatment is given of these subjects, which are essential for making any precise track measurements.

Part II of this work goes on to describe both abstractly and from the standpoint of observation the behavior of the elementary particles whose tracks are seen in emulsion. When appropriate, the information has been made quantitative by the use of the relevant mathematics. Relativistic equations, which are essential to describe high-energy interactions, are used habitually; the kinematic relations of importance in the study of elementary particle processes are introduced.

Separate chapters are devoted to neutrons, and to electron and photon processes. Criteria for particle identification from their tracks in emulsion based on the techniques given in Part I are discussed. Applications in cosmic ray physics, nuclear physics, biology, and earth sciences are cited. Attention also is given to experimental procedures in the use of accelerator sources of high-energy particles.

The book by Powell, Fowler, and Perkins is the only modern one in the English language that encompasses any of this area of knowledge. Their work is recommended to the reader as a splendid atlas of emulsion photomicrographs. Its purpose, however, differs from that of this book which undertakes to provide information that is necessary for the efficient utilization of emulsion as an instrument.

For this work, the writer has drawn on all available experience he has gained from visits to most of the important emulsion laboratories in North America, Western Europe, the Soviet Union, and Asia. He also attended the international conferences specifically devoted to the topic of nuclear research emulsions and the many other conferences on related subjects. It is a personal document to the extent that it may reflect a part of the writer's approach to science—a respect for, perhaps a preoccupation with, exact detail.

Berkeley, California
January, 1963

WALTER H. BARKAS

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Miss Olga Fekula assisted on many occasions by translating items of information from the Russian language into English.

Dr. H. H. Heckman has constructively reviewed parts of the manuscript, and, indeed, the work owes much to the criticism of all the writer's associates. They, including both physicists and scanners, have been invaluable sources of practical information, and each has been ready to lend a hand in whatever way he could. Perhaps more than any other individual, Miss Frances M. Smith has taught the art of emulsion observation. To her measurement skill the development at the Lawrence Radiation Laboratory of emulsion as a precise instrument owes much.

Thanks are due Professor P. Cüer for extended discussions on the topic of silver halide sensitivity, for his personal friendship, and for his leadership in promoting understanding of the emulsion instrument.

All in this field must be appreciative of the part played by C. Waller in producing emulsions of the quality now available, and for his practical cooperation.

The huge task of typing the manuscript and organizing the references was undertaken cheerfully by Evelyn Gray, and very competently finished by Barbara Bole. To them, and others who helped, I am deeply grateful.

WALTER H. BARKAS

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CHAPTER 1

Emulsion as an Instrument of Research

1.1 Tasks for Emulsion

Much of the effort of modern experimental physics is devoted to bringing within man's ken the invisible, inaudible, and otherwise unsensed world of atomic and subatomic processes. Means for doing this by which the paths of electrically charged particles are made visible have proved to be among the most useful. For this purpose special silver-halide emulsions,* which constitute the subject of this book, have been found extremely versatile. When correctly used, they also permit accurate measurements to be made on elementary processes.

Silver halide emulsion of the type used for registering the tracks of charged particles consists of about equal parts by volume of halide crystals, a few tenths of a micron in diameter, and a matrix material which is chiefly gelatin. An ionizing particle on encountering a crystal may render it developable. After development, followed by fixing and washing to remove the undeveloped crystals, the gelatin is transparent. With a microscope the paths of charged particles that penetrated the emulsion are visible as trails of minute silver grains. A true three-dimensional image is produced. The paths of particles, outlined by silver, literally exist in space.

1.1.1 Emulsion as an Instrument of Exploration

On April 7, 1959 a rocket carried a package containing various instruments into the lower of the Van Allen radiation belts. The existence of this belt of radiation was known at that time, but its nature was not. The nose cone was recovered. In it were a few postage-stamp size pieces of nuclear research emulsion that had a story to tell. During the 15 min that the rocket remained at an altitude above 1000 km, the emulsion had gathered rather complete information about the radiation.

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* The author prefers the descriptive names "nuclear track emulsion" (German: "Kernspuremulsion") or "nuclear research emulsion" to the ambiguous expression "nuclear emulsion," which is frequently used.

Proton tracks in the emulsion definitely established the nature of the ionization that had been detected previously. Freden and White (FW 59), at the Livermore branch of the Lawrence Radiation Laboratory, analyzed the tracks. They determined the proton energy spectrum, the flux density, and observed that other types of nuclei were almost completely absent. This experiment is a good example of the peculiar fitness of emulsion for exploratory investigations.

Of importance in this application was the incredible "compactness" of emulsion. Only a tiny volume subjected to irradiation is sufficient to provide a rather complete analysis of the radiation traversing it. It further has the capacity of "memory," so that all the protons that traversed the emulsion at any time during the rocket's flight were recorded.

Because of its memory, emulsion can be considered to have extreme sensitivity. For example, it would not be difficult to detect a flux of low energy antiprotons amounting to 10^{-7} per square centimeter per second, although a long exposure time would be necessary. On the other hand, it has an enormous range of linear response. A flux of a million particles per square centimeter is also accurately measureable, even if they all arrive in a small time interval. Simultaneously, emulsion has good discrimination. An experienced observer is often able to find tracks of a particular particle type when unwanted tracks outnumber those sought by a million to one.

Emulsion is used to detect charged particles, and at the same time it measures their energies more accurately than other detecting devices. Both of these features are important in an instrument that is used for exploration and analysis. They were necessary for the rocket experiment.

With regard to temperature, emulsion has an extreme operating range. From liquid helium temperature to the boiling point of water is the approximate range in which it has been used.

To suggest other roles that emulsion can play, we may recall a few of its applications for exploration. In May 1947, Lattes *et al.* (LMOP 47) published a paper in *Nature*. It was an account of some extraordinary events recorded in the then new Ilford C. 2 emulsion plates. They reported the observation of a meson that came to rest in emulsion and became the origin of another meson—a heretofore unheard of process. They even were able to estimate the masses of the particles involved. In the same paper they confirmed observations of the emission of mesons from nuclei and disintegrations of nuclei by mesons which had previously been observed by Perkins (P 47) and by Occhialini and Powell (OP 47). These processes were illustrated by excellent photomicrographs. In the pictures were displayed the characteristic behavior patterns of the elementary particles that are now known as π mesons.

FIG. 1.1.1. Photomicrograph of a negative π meson track produced in C.2 emulsion during the course of the experiment leading to the first artificial production of π mesons. (Photomicrograph by A. Oliver.)

In the following year Gardner and Lattes (GL 48) placed emulsion within the vacuum chamber of the 184-inch cyclotron of the University of California and detected for the first time mesons made by an accelerator. A photomicrograph from their historic paper is shown as Fig. 1.1.1.

In balloon flights to altitudes above 90,000 ft, Freier *et al.* (F — P 48) observed that heavy atomic nuclei of great energy were bombarding the upper atmosphere. The existence of heavy primary cosmic radiation was proved in this experiment by the use of emulsion detectors, and was further substantiated by a small cloud chamber.

In quite another area, NIKFI type A emulsions are carried to remote places in Siberia to provide a simple means for the assay of the radioactive isotopes in rock specimens (B 56).

O'Ceallaigh (O 51), in attempting to measure the electron decay spectrum of μ mesons in emulsion, found the track of a secondary particle that had an anomalous multiple scattering sagitta. He was able to show it represented a new decay mode of a heavy meson. At that time, however, it was not known that all the numerous decay modes observed were alternative channels of a single meson. This came later when, with magnetic analysis, the ranges in emulsion of all the K-meson types were found to be the same (HSB 55).

In 1953 Danysz and Pniewski (DP 53) observed a star induced by a fast singly charged particle from which was emitted a prong of range 90 μ, probably an isotope of boron. It was remarkable because on coming to rest it disintegrated violently. At least 120 Mev were released in the disintegration. This large energy release was not compatible with any known behavior of boron nuclei. It was suggested by Danysz and Pniewski that this boron nucleus might be a new form of nuclear matter containing—in addition to protons and neutrons—a hyperon. Their interpretation subsequently was verified and such nuclei are now called hyperfragments.

In yet another application, Perfilov (P 39) and Myssovsky and Jdanov (MJ 39), as early as 1939, were able to detect the fragments of uranium fission with emulsion despite the presence of a large flux of alpha particles.

A French war prisoner in Germany was given a thorium compound for making roentgenograms of his intestinal track. Later he died, and his liver was found to be badly damaged. Five-micron sections of the liver stained with glychemalun were studied using the technique of track autoradiography. The accumulation of thorium in liver "macrophages" was proved by the alpha-particle tracks that emerged from these sites.

For tracer work and improved autoradiography in medical sciences, for analytical chemistry, for metallurgy, and plant physiology, emulsion has interesting possibilities; in earth sciences, including mineral prospecting, numerous applications have already been made.

An indication of the usefulness of emulsion as an instrument of discovery is given by Table 1.1.1. In it are listed the elementary particles found since 1946 when emulsion came into use for such investigations.

TABLE 1.1.1

MEANS EMPLOYED FOR DISCOVERING NEW PARTICLES

Particle	Instrument
π^+	Emulsion
π^-	Emulsion
π^0	Counters and emulsion
Λ	Cloud chamber
K^+	Emulsion
K^-	Emulsion
K^0	Cloud chamber
Σ^+	Emulsion
Σ^-	Cloud chamber
Σ^0	Bubble chamber
Ξ^-	Cloud chamber
Ξ^0	Bubble chamber
$\bar{p}$	Counters
$\bar{n}$	Counters
$\bar{\Lambda}$	Emulsion

All the particles listed in Table 1.1.1 except the Σ^0 and Ξ^0 hyperons have been seen in emulsion, and therefore might well have been found first with it. There are, of course, many elements of chance in particle discovery, and the probability of success also depends very much on the dollars of effort expended in the search.

Of the particles assigned to emulsion some probably were seen first in cosmic radiation detected by cloud chambers. However, inaccuracies of measurement and a multiplicity of decay modes caused great confusion until precise emulsion measurements disentangled the masses and decay modes. Nevertheless it should be pointed out that emulsion has no great advantage when one is looking for a particle of predicted properties. It is of greatest use for discovering utterly new things, the anomalous behavior of which often can be recognized unambiguously from a single event. Thus, for example, the τ meson was established firmly by a single event (B-R 49), despite the fact that it took a long time to find another example of this decay mode.

The track of a particle in emulsion constitutes its signature. The character of the particle—its charge, mass, velocity, and interaction behavior—can be derived from a microscopic examination of the track. If a track or a track configuration looks unfamiliar to a trained observer, so that he is not able to identify it at once, the event may merit serious study. For an experienced observer the scattering, rate of change of grain density near the terminus, and terminal behavior characterize the particle.

Neutral radiations such as neutrons, π^0 mesons, K^0 mesons, and hyperons also can be studied with emulsion because they interact with nuclei, they decay into charged particles, or the products of their decay interact. Photons are observed by means of the electrons produced by the photoelectric effect, the Compton effect, and especially by pair formation. They are also studied by means of induced photonuclear processes. The photodisintegration of the deuteron in deuterium-loaded emulsion is particularly useful. The photon energy, flux, direction, and polarization can all be deduced from analyses of the electron and proton tracks visible in the processed emulsion.

Nuclear research emulsions can be loaded with many materials so that particles traversing the emulsion can be caused to interact with nuclei other than those normally present. In particular, the emulsion can be loaded with deuterium, or the concentration of normal hydrogen and oxygen can be increased. It can be loaded with Li^6 for use as a neutron spectrometer or with heavy elements for fission studies. Normal emulsion contains both light and medium-weight elements, so processes involving either kind of nuclei can be studied. It is an ordinary kind of matter, and the processes taking place in emulsion are typical as those occurring in other solid condensed matter. In emulsion the whole sequence of events taking place in the body of the material is made visible. The trajectories, moreover, are preserved in the gelatin permanently so that the events can be restudied at any time, from any aspect.

Standard emulsion contains about 0.053 gm/ml of hydrogen. This is about the same as the density of liquid hydrogen. For the study of reactions and interactions with free protons, emulsion competes even with the liquid hydrogen bubble chamber, and it does certain things the bubble chamber cannot do.

Not the least important feature of emulsion is that as an instrument it is relatively cheap, and may be contained in a small volume. It, therefore, is very useful for survey work. For studying high energy processes, emulsion has a great advantage in economy compared to other methods. It is, in the first instance, very sparing of machine time when an accelerator is used. The cost of the emulsion itself is seldom as large as the cost of the equipment and supplies generally required for other experiments. Also, each exposure usually has many by-products, or by-product studies that could be made. Institutions with small research funds can participate in important investigations by using emulsion detectors. Possibly there is no scientific institution so small, so remote, or so restricted in facilities that it could not carry on significant research using emulsion detectors. For many problems the costs are no more than those incurred by an amateur photographer in pursuit of his hobby; amateur workers with nuclear track plates, akin to amateur photographers, amateur astronomers, and radio "hams," are to be expected.

The special characteristics of the emulsion instrument have made it a means for cooperative conduct of high-energy research. Irradiations can be made with large accelerators, in balloons, or in rocket flights. Subsequently, the emulsion may be analyzed thousands of miles away, perhaps in several countries.

Emulsion approaches the ideal as an instrument for the explorer partly because of its versatility. As we have noted it is used on the one hand to discover new elementary particles, on the other to study the occlusions in rocks. It is a detector and analyzer of the disintegration products of nuclear reactions. With it we observe the interactions of nuclei with nuclei, and witness the decay of unstable particles. We can determine by studying the tracks produced in emulsion the number, direction, character, and energy distribution of any type of charged particle. Even the neutral particles can be detected and studied through their interaction behavior and their decay into charged particles.

1.1.2 Emulsion as an Instrument of Measurement

The masses of several elementary particles have been measured in emulsion immediately after their discovery. For many of them, the emulsion measurements remain the best. One reason for this is that in emulsion it is possible to measure the true rectified range of the particle. It is also usually possible to determine the magnitude and direction of its velocity, the rate of change of its velocity, the product of its velocity and momentum, and its moderation time. Its reaction or decay behavior likewise may constitute important observable data. The density of tracks can be observed and reaction cross sections calculated from this information.

By magnetic bending external to the emulsion, or even by bending in the emulsion itself, particle momenta can be measured. Usually very good precision can be achieved with an external field because extreme accuracy of distance and angle measurement is possible (BBS 56).

Such a variety of methods for energy measurement has been developed, that one has usually two or three means available for any event, and the total energy interval of protons, for example, in which measurements can be made extends at least from 0.1 Mev to 4 Bev. Because of the high stopping power of emulsion and its short radiation length, huge electromagnetic cascades also can be contained in a large stack, and the complete development of the cascade and its final degradation can be witnessed.

Quite another application of nuclear research emulsions has been made to the problem of radiation monitoring for the protection of people who work with radioactive materials, X-ray generators, and high-energy accelerators. Emulsion is absolutely unique in the ability of a few cubic millimeters of it to provide a quantitative analysis of all harmful radiations present.

Owing to the high stopping power of emulsion, a large fraction of even such short-lived particles as hyperfragments and Σ^+ hyperons are brought to rest in emulsion before they decay. Their ranges and moderation times are then easily measured.

Good lifetime measurements of most of the unstable elementary particles have been made in emulsion, and the partial disintegration rates of some decay modes have been evaluated only in this way (N-B 59). Emulsion has been used to measure time intervals even as small as 10^{-16} sec.

Perhaps the most reliable neutron spectroscopy in the 1-15 Mev region is done with emulsion detection. For magnetic spectroscopy of alpha particles, and other nuclear fragments, the accuracy and sensitivity of emulsion detectors is often exploited. The angular resolution obtainable with emulsion detection is unsurpassed.

Despite these remarkable things that can be accomplished with emulsion, its use as a quantitative instrument, rather than as a mere detector, is difficult. The correct measurement of energies, masses, etc., requires exact knowledge of the instrument itself.

1.2 Limitations of Emulsion

Emulsion cannot be used intelligently without a correct assessment of its deficiencies as well as advantages as a detector. A number of these also are common to all visual detectors.

One of the important imperfections is that its composition cannot be changed arbitrarily, so interaction studies in emulsion are limited to those with nuclei normally present and those others with which the emulsion can be loaded (with some difficulty, and in only limited concentrations). The presence of several different nuclear types in the emulsion makes it difficult and often impossible to determine for a specific interaction event what nucleus was involved. Sometimes it is possible merely to be sure of the group (Ag, Br, I), (C, N, O), or H; in other instances even such a classification may not be possible. Usually, however, the hydrogen reactions are quite distinctive, and often reactions with light nuclei, especially carbon, are recognizable.

The minuteness of the volume in which phenomena must be analyzed is sometimes a disadvantage, because often one is working at the limit of resolution of the best microscope objectives. It also means that correlated events only a centimeter or so apart are very difficult to find.

The immense numbers of unrelated tracks that accumulate as "background" in emulsion because of its continuous sensitivity often destroy the usefulness of an otherwise successful exposure. Old background tracks in a stack, however, in most cases can be detected and eliminated by shifting the pellicles just before the exposure so that old tracks cannot be traced into adjacent pellicles. The tracks which accumulate in the emulsion prior to the exposure also can be eliminated or reduced by using fresh emulsion, by employing a rapidly fading emulsion, or by using accelerated fading or eradication of the latent image. The emulsion has one other means for distinguishing between the "wanted" and unwanted tracks so as not to record them all indiscriminately. It can be hypersensitized just before exposure.

In thick layers of emulsion, light scatters from the background tracks, from fog grains, from foreign material, and from colloidal silver. This reduces the contrast of tracks deep in the emulsion. The short working distance of high-power objective lenses as well as processing difficulties also limits the thickness of emulsion layers that can be used. Observations on long tracks must therefore be carried out in emulsion stacks of many pellicles, with attendant complication.

For particles at the minimum of ionization, the generally available materials have been marginal with regard to sensitivity. Often a "minimum" track has been difficult to see and follow—sometimes it has been impossible. Recently hypersensitization has largely overcome this difficulty. On the other hand, the best available emulsions from the point of view of sensitivity lack discrimination, and the tracks of all highly ionizing particles are saturated. This difficulty is not insurmountable and emulsions of higher sensitivity along with better discrimination are possible and are being developed.

Emulsion, which has a gelatin base, is subject to distortions which affect range and angle measurements. Distortion is a particularly serious source of error in multiple scattering measurements. The thickness of the emulsion, both processed and unprocessed, varies with the relative humidity. This may be a serious drawback for accurate measurement. Unless good technique is exercised, mounted emulsion pellicles often suffer from blisters. The unmounted pellicles are not mechanically strong and rigid, especially when warm and damp, so that dimensional changes are possible in them. A number of processing operations remain at present so critical or awkward as to constitute demerits for the emulsion technique.

Another quite different criticism of the emulsion method of detection is the delay, while the plates are scanned, in obtaining the data. The work of scanning is often tedious and exacting. Care always has to be exercised to avoid observer biases and subjectivity in the results. Electronic counting is of course much faster, but it would not be an intelligent application of emulsion to do with it only what a counter can do. Many efforts to carry out electronic scanning have been made, but as yet without great success. Nevertheless some scanning operations are now carried out with semiautomatic equipment and the trend in this direction certainly must be encouraged.

Control of sensitivity is not in a completely satisfactory state—not only is the highest sensitivity often too low, but discrimination is lost when the sensitivity is high. One frequently must choose a low sensitivity best suited for a particular kind of event, and information on other processes taking place in the same emulsion then may be lost. This difficulty is less acute in emulsion than in other track-recording instruments, however.

Emulsion has the disadvantage that the particle tracks are generally so short and their scattering so great that only very high magnetic fields are able to bend the tracks enough so that momentum and sign-of-charge measurements can be made. However, the scattering, which interferes with the bending, itself provides a good measure of the product of the particle momentum and velocity. It should also be remembered that one may usually perform a magnetic analysis prior to intercepting the particles.

Emulsion cannot be used at very elevated temperatures. In vacuum it loses water, possibly spoiling the vacuum and suffering changes in its own density. It is damaged by exposure to light. High mechanical pressure, as from scratching the emulsion surface can render it developable, and often is a source of trouble. Some materials poison emulsion so that it is either blackened or the latent image is destroyed. Active metals such as aluminum in contact with the emulsion react with the silver bromide, but this can be slowed by lowering the temperature. Oxidizing agents destroy the latent image, and stains are often produced in the emulsion by impure chemicals or oxidized developer.

The processing of thick layers of emulsion is not easy, and unless good technical skill is exercised, nonuniformity of development can lead to serious errors of measurement and of interpretation.

Other troubles with emulsion include reticulation and shearing that take place in the emulsion when solution temperatures are too high or when the solution concentration changes rapidly. On the other hand, when the emulsion is too dry it tends to strip off its glass backing, or if unmounted, it curls and wrinkles.

For production experiments in which the detector must also be the target, emulsion is at a disadvantage. In complex nuclei the elementary-particle processes are distorted and obscured by secondary effects. To avoid this difficulty, hydrogen-filled targets with external detectors such as emulsion, counters, or hydrogen-filled cloud chambers have been used in the past. At present the hydrogen bubble chamber is the best instrument for this purpose.

The very versatility of emulsion may become a defect because some requirements are incompatible with others. The presence of atoms of high atomic number in the emulsion makes the multiple scattering technique possible, but interferes with the precise measurement of particle direction. On the one hand, its continuous sensitivity makes it good as a monitor, on the other it destroys its time discrimination.

A fairly large number of false "discoveries" have been made by workers with emulsion. It is worthwhile to study these as case histories in order to ascertain how and why the mistakes were made. In reviewing the episodes known to the writer the reasons seem to be of two sorts. The first has nothing to do with emulsion as an instrument. It has to do mostly with the scientific competence of the observer. It may involve too great a desire to find the process in question, or an incomplete understanding of statistical fluctuations—particularly when small numbers are involved. Occasionally, merely bad luck with statistics will cause a competent observer to be mistaken for a while. Unknown biases are always possible, as are mathematical mistakes.

In the other category are errors made because of an incomplete mastery of the instrument. Emulsion research has a deceptive appearance of simplicity; some operations are indeed simple. The danger arises when someone with superficial understanding attempts quantitative studies. Measurements of ionization, multiple scattering, angle measurements, and accurate range measurements are not for amateurs. For this reason, much of this book is devoted to detailed treatments of these subjects.

One must be particularly on guard against nonuniform development, fading, distortion, background, and pellicle misalignment.

1.3 Types of Nuclear-Track Emulsion

Early applications of emulsion to the recording of particle tracks were made with plates manufactured for other purposes. A large variety of fabrication procedures and user requirements now have led to the manufacture of several special kinds of emulsion that will record the tracks of charged particles. In addition to commercial emulsions, the manufacture of a number of noncommercial types has been described in the literature in more or less detail. Tracks in emulsion were already observed early in this century,* and preparation of emulsions specifically for particle track recording was undertaken as early as 1927. However, it was only after wartime projects in England and Canada were independently successful in producing excellent emulsions that great discoveries were made using this technique. With these triumphs, emulsion became firmly established as an instrument of nuclear physics, and further effort has led to the production of improved types of emulsion.

Once a composition and procedure has produced an emulsion meeting a particular set of standards, the reproduction of the same properties in subsequent pourings requires the development of exacting quality control procedures. In order for a commercial emulsion to be sold on the open market, it should meet many conditions that experimental emulsion batches may not satisfy. The quality control must insure that each sample described as an emulsion of a certain type falls within prescribed narrow tolerances in sensitivity, composition, homogeneity, density, and grain-size distribution. Furthermore, the emulsion surfaces must be smooth, and the layers of uniform and specified thickness. The problems of undistorted mounting, processing, shipping, and storage of thick emulsion pellicles should have been solved, and the density of fog grains, radioactive contamination, and foreign material

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* The history of the development of the emulsion method of recording charged-particle tracks is interesting. By now, however, many have contributed to the manufacturing, exposure, and processing techniques. Besides, a considerable fraction of the information is unavailable for commercial or political reasons so that a correct perspective seems unobtainable. Among the pioneers whose contributions are unquestioned one may name: M. Blau, D. M. Bose, P. Demers, A. Jdanov, S. Kinoshita, N. A. Perfilov, C. F. Powell, M. Reinganum, E. Schopper, H. J. Taylor, H. Wambacher, and T. R. Wilkins. The interested reader is directed to the rather large amount of historical information given in the survey articles and books cited in the bibliography.

in the gelatin cannot exceed very low limits. The stability of the latent image also must be controlled, and be adequate for the applications to which the emulsion is to be put.

In classifying emulsions we have relaxed these conditions somewhat, so as to include among commercial emulsions those believed by the writer to be articles of commerce, even though some of the above requirements may not be met fully.

The compositions of nuclear-track emulsions for which data were obtainable are given in Chapter 3. Generally speaking they are much more concentrated than photographic emulsions; about half the volume is taken up by the silver halide crystals.

1.3.1 Commercial Emulsions

In Table 1.3.1 are tabulated a number of emulsion types. There is reason to believe that they can be made by the manufacturers listed in the last column, although currently some are not in production. Many emulsions that are now obsolete, but probably could be made, have been deleted. The grain sizes listed in some cases are estimates. While the price of emulsion is not a cognizance of this work, ten dollars per cubic inch is the order of magnitude of the cost of pellicle emulsion in 1960.

The emulsions in Table 1.3.1 ranging from left to right, are placed in order of decreasing sensitivity. This arrangement has been suggested by the system of Ilford Ltd. Type 6 we reserve for emulsions hypersensitized so that minimum ionizing tracks contain more than 50 grains per 100 μ. Hypersensitized emulsions are prefixed by an H. Type 5 will record relativistic particles, and type 4, also, but marginally. Low-energy electron tracks are recorded in type 3, and, at best, only electron ends in type 2. Alpha particles are well recorded, and proton- and meson-endings can be seen in emulsions of types 1 and 0. The negative numbers are reserved for emulsion made to eliminate the tracks of all but multiply charged nuclei.

The following firms and institutes are known to have made or are successfully making nuclear research emulsions. The individuals responsible, or the persons reporting the emulsion characteristics are also mentioned.

Ilford Ltd., Ilford, London, England

This firm (Cecil Waller, Chief Chemist) has been the most important commercial supplier of emulsion. Special production requirements of experimenters have frequently been met, and a variety of well-proven

TABLE 1.3.1

COMMERCIAL EMULSION TYPES

Grain Diameter (μ)	Relativistic particles			Medium and low energy protons				Fission fragments and other heavy ions			Maker
	6	5	4	3	2	1	0	−1	−2	−3	
0.27	HG.5	G.5	G.4	G.3	G.2	G.1	G.0	G. −1	G. −2	G. −3	Ilford
0.20	HK.5	K.5	K.4	K.3	K.2	K.1	K.0	K. −1	K. −2	K. −3	Ilford
0.15	HL.4	—	L.4	L.3	L.2	L.1	L.0	L. −1	L. −2	L. −3	Ilford
0.4	—	NTB-4	—	—	—	—	—	—	—	—	Eastman
0.3	—	NTB-3	—	NTB-2	NTB	NTA	—	—	NTC	—	Eastman
0.28	HR	R	MP	—	—	—	—	—	—	—	NIKFI
0.16	—	—	MK	K	Я-2	—	A-1,2	—	—	—	NIKFI
0.18	—	—	—	—	—	T-3	T-2	T-1	—	—	NIKFI
0.08	—	—	—	—	—	—	—	—	0	—	NIKFI
0.28	P-R$_1$	P-R$_2$	P-R$_3$	—	—	—	—	—	—	—	RIAN
0.09	—	—	—	—	P-9$_s$	—	—	—	P-9$_0$	—	RIAN
0.26	—	ET-7a	—	ET-6B	—	—	ET-2E	—	—	—	Fuji
0.3	—	—	—	K.2	—	—	—	—	—	—	Agfa-Wolfen
0.3	—	NT-4	—	NT-2a	—	NT-1a	—	—	—	—	Kodak Ltd.
0.07	—	—	—	NUC3.07	—	—	—	—	—	—	Gevaert
0.15	—	NUC3.15	—	—	—	—	—	—	—	—	Gevaert

emulsion types are available. Excellent quality control is exercised. Emulsion pellicles of up to 2000 μ are manufactured, and stacks of 50-100 liters of 600 μ emulsion have been made. Plates with emulsion up to 1000 μ in thickness can be ordered. Recently, small lots of excellent hypersensitized L.4 and K.5 emulsion have been prepared. It is also possible for the user to carry out the hypersensitization (Chapter 4). Emulsions of fixed composition, but of various grain sizes and sensitivities are available. The ratio of gel to halide can also be varied, and emulsions with 2, 4, and 8 times, the normal gel content have been sold. Ilford emulsions can be obtained in gel form for pouring by the user. Special mountings of emulsion on plastic bases have been available, and various loaded emulsions are marketed. Ilford has been perhaps the most successful establishment in producing a good bond between the emulsion and the glass plate on which it is mounted.

The development of concentrated emulsion by Ilford was strongly influenced by Professor C. F. Powell. He also used the products made by Ilford Ltd. and Kodak Ltd. so effectively in cosmic ray research at the University of Bristol that he received a Nobel prize.

Not listed in Table 1.3.1 are many older types of Ilford emulsion, perhaps the most famous of which was their emulsion C. 2, which was the predecessor of type L.2. Emulsion types B, C, D, E, and F were sold with various sensitivities up to 3.

Eastman Kodak Company, Rochester, New York. (*J. Spence, J. H. Webb*)

This company has retained an interest in the manufacture of nuclear research emulsions for many years. Pioneer work on such emulsions was done at least as early as 1931 in cooperation with T. R. Wilkins, who recorded alpha particles in emulsion, and in 1935 used emulsion for detecting cosmic radiation in a high altitude balloon flight.

Several emulsion types of various sensitivities are made currently. All nuclear-track emulsion manufactured by the Eastman Kodak Company, except type NTC are available as plates of 25, 50, 100, 150, and 200 μ thickness, and as pellicles of 250 μ thickness. Type NTC is sold as plates of 25 and 50 μ thickness. NTA, NTB, and NTB-2 plates are also supplied in a thickness of 10 μ, and in addition NTA and NTB are sold as plates coated with a 5 μ emulsion layer.

Kodak plates can be supplied with or without a protective coating of gelatin on the surface of the emulsion. The coating, which has a thickness of 1/2 to 1 μ helps to protect the surface, but, of course, the portion of a particle trajectory in the coating is not visible. An information bulletin dated August 1956 from the Special Sensitized Sales Department of Eastman Kodak states that the adhesion of their processed and unprocessed emulsion layers (which formerly was not good) has been substantially improved. In making these improvements the chemical compositions of the emulsions were altered.

Kodak nuclear-track plates, films, and pellicles are sealed in moisture-proof envelopes. The manufacturer advises, when using only a portion of the contents of an envelope, that it be resealed. The recommended storage conditions are 40°-50° F and 50% relative humidity.

In 1962 a new emulsion NTB-4 was put on the market. It is of excellent sensitivity. (It is also more sensitive to light than other nulcear research emulsions.) Its density is close to that of normal Ilford emulsions. Iodine is not listed as one of its chemical constituents, and the latent image stability is improved. The emulsion is sold in kits consisting of 600 μ pellicles, gel-coated glass plates, and mounting gelatin. Standard sizes in which pellicles are sold are 3×4, 4×4, and 4×6 inches, but special requirements can also be met.

NIKFI Institute, Moscow, USSR

This Institute (Director: Vladimir Uspensky) carries on a broad program of research in photographic recording. A department (Head: Constantine Bogomolov) of NIKFI was organized in 1949 to attempt to make nuclear research emulsions similar to those made by Ilford Ltd. Groups devoted to coarse grain emulsions, to fine grain emulsions, as well as an important colloid section (Head: V. M. Uvarova) form the research organization. Test groups consisting of an irradiation group which has a betatron for its chief tool, a group for development and microscopy, and one for analysis are also part of the organization. An experimental manufacturing plant makes the emulsion. NIKFI emulsion type R was successfully developed with properties very similar to those of Ilford G. 5 emulsion. It was reported in 1958 (B-D 58) that this emulsion could be hypersensitized by triethanolamine (see Chapter 4), and the emulsion made more sensitive than any other produced, up to that time. Other less sensitive NIKFI emulsions are designated T-1, T-2, A-2, Я-1, Я-2, and K.

A new emulsion, type M, with a mean grain diameter of 0.14 μ has recently been described by Sirotinskaya *et al.* (SBD 62). Normally 30 grains per 100 μ are developable in relativistic tracks and, when the emulsion is hypersensitized, as many as 50 to 60. This emulsion has been found useful for making tritium microautoradiograms.

The NIKFI emulsions have a rather unform grain size obtained by lamellar centrifugation; the centrifugation also permits the precipitation of the halide to be carried out in dilute solutions. The fog or single grain background in these emulsions is low. The NIKFI emulsions are made with a special gel material, largely processed gelatin, but containing plasticizers which give it improved colloidal stability and good mechanical properties. This has been an achievement of the colloid group (UM 58) (MU 60).

NIKFI emulsion adheres well to ordinary glass if the glass is treated as directed, and if the other steps of mounting are also carried out carefully (see Chapter 4).

Fairly large stacks of 400 μ NIKFI emulsion have been made. The emulsions are also supplied to users in the form of liquid emulsion. The emulsion T-1 may be prepared loaded with lithium acetate or deuterium. The plates A-2 are glass-backed layers of emulsion of thickness 50-100 μ in which the latent image of an alpha particle does not fade during months of exposure or storage.

Emulsion recording of charged-particle tracks in Russia did not begin with NIKFI. Genuine and important pioneering work in this field took place many years earlier. Myssowsky and Tschishow (MT 27) in 1927, and work by Jdanov (J 35) and others in the third decade of this century established an honorable tradition.

Radium Institute of the Academy of Sciences (RIAN), Leningrad, USSR

Emulsions with very small grain diameter and with extraordinary sensitivity are produced by Perfilov and his collaborators (PNP 57). The grain diameter is so small that some samples transmit red light. It is possible to use these emulsions without fixation and consequent distortions. Photomicrographs of alpha-particle tracks in developed but unfixed emulsion, as well as of tracks of particles with a grain density of 60 per 100 μ at minimum have been published (PNP 57). Some details of the method of manufacture of these emulsions also have been given.

In production it has been found possible to add large quantities of heavy elements such as lead or tungsten to these emulsions (BZNP 60).

No use of thick layers or stacks of these emulsions is known. P-9 plates of 60 μ processed thickness have been employed by the writer. A resolvable grain diameter of approximately 0.35 μ was found after development in D-19 developer. The single grain background was less than 1 per 1000 cu μ.

In Table 1.3.1 the grain sizes of the emulsions listed have been estimated. It has been stated (P-D 58) that the developed grain sizes of the emulsions P-R, P-9 and P-9_0 are $0.32 \pm 0.04\ \mu$, $0.29 \pm 0.04\ \mu$, and $0.26 \pm 0.05\ \mu$, respectively.

The density of the RIAN emulsions is somewhat less than those of Ilford, and the stopping power correspondingly lower.

Fuji Films Ltd., Tokyo, Japan (*K. Imaeda, M. Kazuno, S. Fujisawa, Y. Koseki, A. Miyauchi, and Y. Takao*) (I-T 58)

In 1957 an emulsion ET-7A sensitive to relativistic particles was developed from the older types ET-2E and ET-6B. Both plates and pellicles are now manufactured. The density, composition, and grain size are very much the same as Ilford emulsion G.5. An emulsion NREI by Sakura of Tokyo is similar.

Kodak Ltd., Harrow, England (*W. F. Berg, R. W. Berriman*)

While Dr. Berriman was the first to make an emulsion that recorded relativistic particle tracks, this emulsion NT-4 was never produced in quantity. Several other emulsions were marketed at one time, but it is believed that they are not made currently.

Filmfabrik Agfa-Wolfen (*Karl Lanius*) (L 53)

The emulsion K. 2 has been manufactured on glass plates in layers of 110 μ thickness. The latent image tends to fade in a month or so. It is sensitive to protons of about 150 Mev. From the saturation behavior of the grain-density curve, the emulsion grain size is about average. Emulsions also have been made by Agfa-Leverkusen.

Gevaert Photo-Producten N.V., Antwerp, Belgium

Two new nuclear research emulsions have recently been marketed by Gevaert: Scientia "NUC 3.07" and Scientia NUC 7.15." The emulsion designated NUC 3.07 is extraordinary for its extremely small grain diameter. The one designated NUC 7.15 provides the highest advertized sensitivity available in any emulsion—50 grains per 100 μ in relativistic tracks. It also has a small grain diameter—0.15 μ. The Gevaert emulsions are sold in all forms—gel, plates, and pellicles. The plates are 1 × 3 inches, the pellicles normally 13 × 18 cm. Many thicknesses are available, and glass plates are supplied with a special substratum for providing a good bond to emulsion.

1.3.2 Noncommercial Emulsion Makers

A number of commercial establishments have experimented with nuclear-research-type emulsion, but have not marketed them in quantity. Valuable contributions to the art nevertheless have been made by workers with these emulsions. For example, Tsien and Cüer (TC 43) reported on the characteristics of the emulsions "Lumiere Micro" and "Lumiere Tous Noirs." Many emulsions quite useable for nuclear-track recording also have been made in the course of experiments on the fundamentals of silver halide sensitivity or to produce emulsions with properties unavailable commercially. For example, Jenny (J 51) very early made an electron-sensitive emulsion.

Various emulsions have been produced in the "Laboratoire de Physique Corpusculaire" in Strasbourg, particularly by Simon (S 58). His work has included studies of sensitization by mineral agents such as gold, rhodium, and sodium hyposulfite.

Emulsions were made by Kubal (K 58) to study the effects of cadmium and iodine ions.

Narath and Heimann (NH 58) used dilute solutions to improve the control of the silver halide precipitation. They developed a method for discarding the excess water by alcohol reprecipitation.

Jean Colomer (C 60) recently has carried out work of originality and probably great significance for the future of nuclear-track emulsions. He has been successful in making emulsions by combining colloidal silver and gelatin. The silver was subsequently brominated with bromine water, and triethanolamine added as a sensitizer. When developed in ID-19 developer, the tracks of the alpha particles and protons were clearly seen and there was no fog. The peak of the grain-size distribution was at 0.03 μ and the bulk of the crystals had diameters in the interval 0.0125-0.05 μ.

In order to investigate the feasibility of manufacturing very fine-grain emulsion for use, for example, in neutron spectroscopy, Oliver (O 58) built an apparatus at the Lawrence Radiation Laboratory to duplicate the results of Demers (D 54) and Perfilov (PNP 57). By introducing automatic controls to regulate the pAg in precipitation, he was able to study emulsion manufacture under carefully controlled conditions. Fine grain emulsions sensitive to relativistic particles were made.

At the University of Liege, A. Hautot and H. Sauvenier (HS 57) have done many experiments, the starting point of which was a fine grain *primitive* emulsion. Such an emulsion does not change its sensitivity with ripening, and no fog is developable.

Zizic (Z 60) prepared an emulsion similar to the emulsion P-9 of Perfilov. It was transparent to yellow and red light. The emulsion was loaded with enriched B^{10}, so that it was a good detector of neutrons by the B^{10} (n, α) Li^7 reaction. Highly concentrated emulsions also have been made by Markocki (M 58).

H. Gauvin and W. Sebaoun (GS 57) described the production of a fine-grain emulsion in which quite satisfactory tracks were obtained and in which silver chloride was the precipitated halide. With this emulsion they were able to study nuclear reactions of chlorine isotopes in the emulsions.

An emulsion "Forte" P/22 with about the same sensitivity as Ilford

C.2 emulsion has been made in Hungary (MP 57). Emulsions N-2, N-3, N-4, and N-5, having sensitivities about the same as the corresponding Ilford numbers, are made in Peking (HLS 59, LSLH 59).

Unique among nuclear and cosmic ray physicists is Pierre Demers of the University of Montreal, who manufactures his own emulsions for cosmic ray and nuclear research. His contributions to the nuclear research emulsion art probably have been as great as those of any other individual.

He learned early to control the grain size. He introduced triethanolamine as a sensitizer in nuclear research emulsion. (It had been used much earlier in photography.) This has recently had spectacular success in hypersensitizing commercial emulsions that were already highly sensitized by "conventional" means. (The "conventional" means include sulfur and gold sensitization, for example, and others known only to the manufacturing establishments.)

Demers pioneered in producing concentrated emulsions and was the first to succeed in making emulsions of exceedingly fine grain that are at the same time capable of recording relativistic tracks. The demonstration that these two requirements, generally regarded as incompatible, could be met simultaneously was an accomplishment of great significance for the future of the emulsion technique. It had become obvious that better discrimination, improved information density in the track, better multiple scattering data, more efficient utilization of the low energy delta rays, more accurate angle measurements, etc., all depended on obtaining emulsions of finer grain, but the first electron-sensitive emulsions had coarser—not finer—grains than such medium-sensitivity emulsions as Ilford C.2.

In the emulsion of Demers that is sensitive to particles at minimum ionization, the grain diameter is about 0.08 μ before development and 0.15 μ after development. About 15 grains per 100 μ develop in minimum tracks. Only about 1 in 60 of the grains encountered by the particle is rendered developable. When the ionization is greater, up to 400 grains per 100 μ are developed and are separately countable. The fine-grain emulsion of Demers increases in sensitivity for a period of months after it is manufactured, but background tracks usually do not seriously affect even old emulsions. This is because the latent image in the small crystals of silver bromide-chloride used by Demers fades rapidly.

The grains are so small, even after development, that tracks in Demers' emulsions are somewhat difficult to see. As yet he has not developed a method of processing his pellicles that avoids serious linear dimensional changes, and an accurate range-energy relation for his emulsion has not been established. It has been found by A. Oliver that Demers' type of emulsion can be mounted on Ilford's special coated glass. Either plates can be poured on the glass or pellicles can be mounted on it for processing. In either case, it adheres well, and the lateral dimensional changes are avoided.

Professor Demers has also experimented with emulsion prepared without using gelatin as a matrix. He has succeeded in recording tracks near the surface in a silver bromide emulsion with a polyvinyl alcohol gel.

In his book (D 58) Demers gives details of his emulsion-making techniques.

CHAPTER 2

The Latent Image and Its Development

2.1 Silver Halide Sensitivity

For many years the nature of silver halide sensitivity has been one of the most challenging problems of solid-state physics and physical chemistry. No important distinction need be made between the nature of the effect produced in a silver halide crystal by a fast charged particle and that produced by photons, although certain differences of a detailed character exist. Users of nuclear-track emulsion, perhaps even more than other photographers, stand to gain in increased power of their instrument by a more complete understanding of the nature of the photographic process.

There is no reason for complacency or satisfaction with the photographic materials available now for nuclear-track work. They are far from ideal, and many experiments are so difficult or give such marginal results that a very great effort to improve the instrument is justified.

The photographic process itself is derived from an idiosyncrasy of silver halide crystals, but these materials are not by any means the only ones to be photosensitive. The useful effect is this: when a silver halide crystal absorbs energy from photons or moving charged particles incident on it, the microcrystal may be conditioned by this experience so that, under the action of a chemical reducing agent, conversion of the halide to metallic silver will proceed more rapidly than in an unirradiated crystal. This capacity to be "rendered developable" by a small amount of energy is for us the important attribute of silver halide crystals.

The physical condition in the crystal that makes it developable is called the "latent image."

It is well established that the latent image consists of a small quantity of elemental silver (known as specks, germs, etc.) collected at one or more points in the crystal known as "latent image sites." While there is now a large area of unanimity in the interpretation of photographic processes, there is not as yet complete agreement on a number of details of latent image formation, and on the topography and character of the latent image sites.

Before discussing the present status of theoretical ideas on these subjects, we shall recall in Sections 2.2 and 2.3 some of the large body of empirical information, derived from observation and experiment, that is pertinent to our understanding of silver halide sensitivity.

2.2 The Behavior of the Latent Image

The amount of silver in the latent image has been measured in several experiments (M 54). The result is that about 3 atoms is the mean amount of silver in a crystal of 0.1 cu μ volume in emulsion that has received just a threshold exposure, whereas 30 atoms constitutes a medium exposure, and 100 atoms is a heavy exposure.

Svedberg (S 22) found that the number of latent-image sites per crystal was distributed according to Poisson's law when one considers crystals only of a single size. This means that, unless the average number of latent image sites is large, there will be a finite probability that some crystals will possess no sites where a stable latent image can form. Since all but a minute fraction of the crystals in Ilford G.5 emulsion, for example, are developable, the average number of latent image sites must be large.

The silver that collects in latent image specks as a result of exposure to light is called "photolytic" silver. One can broaden this meaning somewhat to include also the silver reduced by the passage of charged particles through the crystal. If the exposure of a crystal is prolonged, photolytic silver may continue to accumulate on that already deposited, and the process can go on to the point that much of the silver in the crystal is reduced. When this condition exists, it is known as the "print-out effect." In the print-out effect, the reduced silver often appears under the electron microscope as an extrusion from a latent image site as shown in Fig. 2.2.1. That the latent image is actually silver has been demonstrated. X-ray powder diffraction patterns of silver halide that have been exposed to light show evidence of metallic silver, while unexposed halide does not. If the silver halide is dissolved in sodium thiosulfate solution, only a silver lattice remains of the exposed crystals. It has also been found that oxidizing agents strong enough to oxidize silver will destroy the latent image. Chemical development of an exposed crystal always starts at a number of discrete points which are identified with the external latent image sites. It is now well established, at least for some crystals, that internal latent image sites also exist. One type of experiment that provides evidence for an internal image is the following: the superficial latent image is destroyed by chromic acid so that the

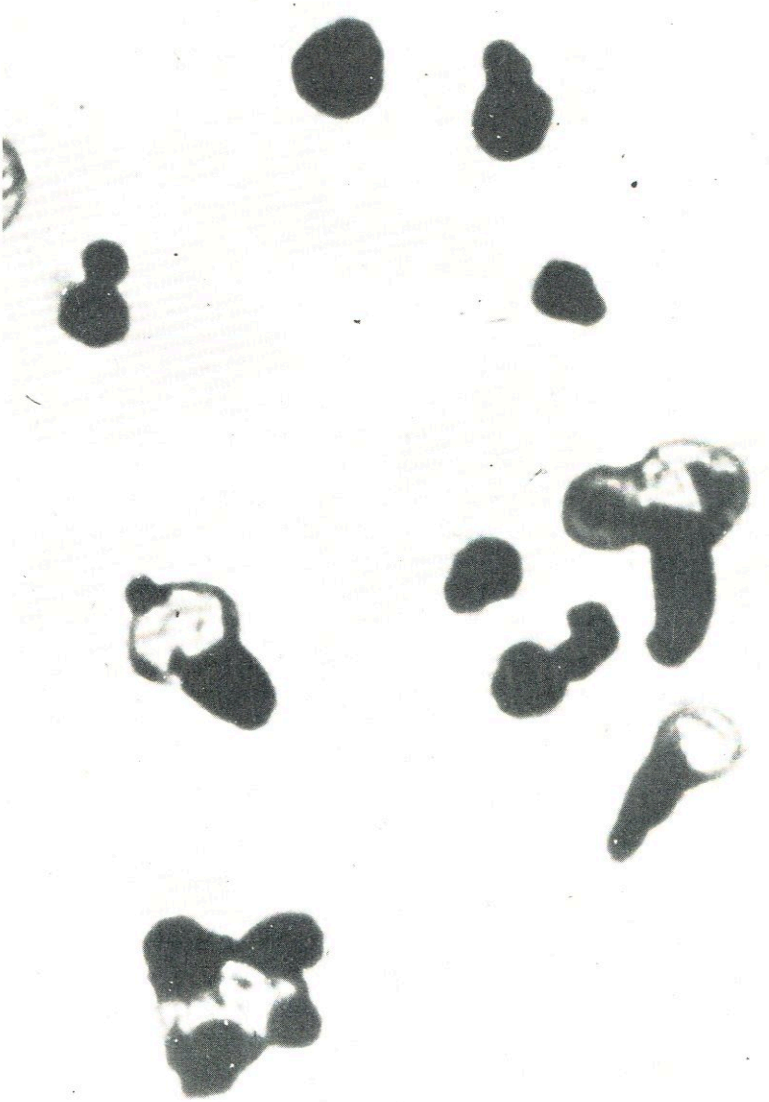

FIG. 2.2.1. Electron micrograph of silver halide crystals after intense electron bombardment. The protuberances on the grains are composed of photolytic silver. (Courtesy of L. Winand.)

crystals are not developable. Then a silver bromide (bromide is the most important halide for photography) solvent such as sodium thiosulfate is used to uncover deeper layers of the crystal. It is then found that the developability of the crystals is restored, presumably because internal latent image sites are made accessible to the developer.

The processes by which the energy of a photon or a charged particle is absorbed in matter lead to the excitation of electrons. A certain threshold energy of excitation (about 2.5 ev) is required before the lowest unoccupied levels can be reached. In these conduction bands the electron can migrate freely through the crystal. The presence of electrons in the conduction bands is confirmed by the observation of electrical conductivity in the normally insulating silver bromide crystals when irradiated. As the electric field is raised the current rises rapidly at first, but then flattens off and saturates at a value proportional to the light intensity. The fact that the current does not rise immediately to the saturation value indicates that electrons are lost in some manner unless they are quickly swept to the positive terminal. It has been established that the conduction bands of massive metallic silver lie about 1 ev below those of the silver in silver bromide, and a silver speck, therefore, can act as a trap for the electrons. In the absence of dyes which shift the spectral sensitivity curve, the threshold photon energy that is strongly absorbed and produces both photoconductivity and a latent image in silver bromide crystals is about 2.5 ev.

Ionic conductivity also occurs in silver bromide crystals, and is attributed largely to the motion of silver ions which occur as Frenkel defects in the crystal. The number of such defects is given by a Boltzmann distribution, and falls rapidly with temperature. Consequently, the ionic conductivity, as confirmed by measurement, must fall as the temperature is reduced.

Thermodynamic considerations can be applied to the formation of the latent image in order to ascertain which alternatives are possible. The result of thermodynamic arguments is chiefly the conclusion that silver, either as isolated atoms or as aggregates of atoms, is unstable in the crystal lattice, but it may collect on external or internal surfaces.

Experiments (HS 51, W 55) establishing in a satisfactory manner that print-out silver and electrons migrate through the crystal, have been made by deflecting the ions and electrons in electric fields. The silver ion mobility at room temperature is such that the time to migrate a distance comparable with the crystal dimensions is about 10^{-3} sec.

The "quantum efficiency" is the number of free atoms of photolytic silver produced per photon in the spectral region where silver bromide absorbs strongly. The maximum value of the quantum efficiency approaches unity, but at liquid air temperatures it is only about 10^{-5}, thus paralleling the ionic conductivity.

The quantum efficiency is not dependent solely on the temperature. It is found that the duration and intermittent character of the exposure also can affect it. If the irradiation is made during either a very short time or over a very long time, the apparent quantum efficiency is less than for the medium exposure times of 0.01 to 1 sec usual for photography. In this time interval one normally finds "reciprocity," the image density being determined by the product, It, of intensity and time of exposure. For exposure times less than 10^{-6} sec no further loss of sensitivity is observed. It is clear that some of the failure of reciprocity at high intensities is simply a matter of recombination of the electrons and positive holes. If n electrons and n positive holes are created simultaneously in a crystal the probability of recombination must increase as n^2. If the exposure is prolonged so that only one electron-hole pair exists at any moment, this loss will therefore be reduced. The loss also goes up with the mean lifetime of the holes. In the Gurney-Mott theory (Section 2.4), high-intensity reciprocity failure was attributed to the sluggishness of the migration of silver ions to a latent image speck so that the migration time (10^{-3} sec) was comparable to or longer than the exposure time.

Low-intensity reciprocity failure can be avoided by a high-intensity preliminary exposure. Subsequent low-intensity exposure contributes to the density of the latent image with complete reciprocity.

At very low temperatures, as for very short times, reciprocity at low efficiency is attained over a wide range of exposure times.

The conditions under which the latent image is produced by fast charged particles differ significantly from those in a typical photographic exposure. First, since the image is usually produced by the passage of only one particle, the exposure time is very short (ca. 10^{-15} sec). This corresponds to an extreme point on the reciprocity curve. Also, the pulse of electric field produced by the passage of a charged particle is equivalent to many photons, some of which have energies far above the threshold for exciting electrons into a conduction band of the crystal. Consequently there must be considerable inefficiency in utilizing the particle field to produce conduction electrons, and the fact that they are all produced in an extremely small time interval again reduces the efficiency because of the reciprocity failure. (It is known, however, that with strong, complete development, short-exposure-time reciprocity failure is less pronounced.) For producing a latent image, most of the energy loss of a charged particle in penetrating emulsion is wasted. Whereas only about 30 ev of energy divided among a few photons is required to produce a developable silver halide crystal, at least 500 ev per developable grain is consumed in producing a particle track. There is obviously much room for improvement in the efficiency with which the energy of charged particles is utilized.

One difference between the effect of a charged particle and that of photons that is not believed to have been considered heretofore is the creation of Frenkel defects by the charged particle. One can estimate the cross section, σ, for transfer of energy exceeding T to a nucleus of atomic number Z_2 and mass M_2 by a particle of mass M_1 charge $Z_1 e$ to be

$$\sigma \approx \frac{2\pi Z_1^2 Z_2^2 e^4 (M_1/M_2)}{T(pv)} \tag{2.2.1}$$

where pv is the product of the momentum and velocity of the moving particle. This formula is valid in the approximate interval

$$10^{-16}/Z_2^2 > \sigma > 10^{-26}(Z_2^{2/3} + Z_1^{2/3})\ \text{cm}^2$$

This means, for example, that if 1.27 ev is the activation energy, the passage of a two-Mev alpha particle through a G.5 crystal typically creates four interstitial silver ions, regardless of the temperature.

For many years it has been known or at least suspected that sulfur plays an important part in silver halide sensitivity. S. E. Sheppard (M 54, S 25) isolated sulfur-containing compounds from gelatin. These compounds increased the emulsion sensitivity to light. He found that many substances containing a thiourea grouping of atoms behaved similarly. Sheppard believed that the sulfur sensitizer was chemically held at the surface of the silver halide grain. Under the influence of heat or change of pH a speck of silver sulfide was thought to form on the crystal surface.

By heat treatment of emulsion in the presence of silver bromide solvent and sensitizing materials the grains are "ripened."

The fine grains in the emulsion are thermodynamically less stable than the large grains. In the process of Ostwald ripening the small grains are dissolved and the large grains grow. This first ripening, the physical one, is carried out generally at an elevated temperature with agitation. The presence of ammonia speeds the ripening. A second maturation, the chemical ripening, takes place during the late stages of emulsion manufacturing. It sensitizes the emulsion but leaves unaltered the grain-size distribution. According to Bogomolov *et al.* (BSDU 57), for a low fog level the rate of chemical maturation must be the same for all grains.

The "principle of homogeneity" of Bogomolov may be translated as follows: "To obtain the maximum sensitivity of an emulsion with minimum fog, the preparation must be carried out in such a way that all the microcrystals have a distribution as uniform as possible of the chemical maturation velocities at all stages of the operation."

In another publication Bogomolov *et al.* (BDZ 56) state that a limited amount of discrimination control can be obtained by varying the length of the second ripening of the emulsion.

Numerous substances added to the gelatin, especially during chemical ripening, are known to produce a heightened photographic sensitivity of the emulsion. Nuclear research emulsions contain so little gelatin that the natural sulfur content may be insufficient for sensitization, and extra sulfur is required. It is noted in this connection that the sulfur content of Ilford emulsions containing extra gelatin varies in proportion to the concentration of halide rather than with the gelatin content.

An additional sensitization with pinakryptol yellow enabled Wambacher and Blau (W 31, BW 32) to record tracks of protons. Many other organic dyes have been used for sensitization.

Some optical absorption bands in dyes originate in transitions of unlocalized electrons of the chain. These electrons are similar to the conduction electrons of metals except that they do not pass from one dye molecule to another.

Generally speaking, the dye molecules have a large Van der Waals attractive force to silver halide crystals and are readily adsorbed. It is necessary for the dye to be adsorbed to the crystal for sensitizing to occur, but this is not a sufficient condition. Other conditions are that the dye absorb energy and that this energy be transferred to the crystal. The energy is utilized by the best sensitizers to produce a latent image almost as efficiently as by the silver halide itself.

A dye permits latent image formation by photons with less energy than the 2.5 ev required to raise an electron of the unsensitized silver halide crystal to a conduction band. It follows that energy transfers of less than 2.5 ev by charged particles penetrating sensitized emulsion can also be utilized to make a developable track.

A mechanism of dye sensitization that accounts for many of the presently known facts has been discussed generally by Franck and Teller (FT 38). Energy of excitation is propagated through a crystal structure or between crystal structures in intimate contact with each other by "excitons" which formally have some of the properties of particles. The energy contained in an exciton which is produced in a dye layer adsorbed to the crystal may be lower than 2.5 ev.

Inorganic materials, gold, thallium, rhodium, cadmium, and tin compounds, are other sensitizers frequently referred to in the literature.

The presence of excess silver in emulsion also may be important for sensitivity.

It need hardly be stated that the theory and practice of photographic sensitization is the most closely held secret of the makers art, and a satisfactory account of it cannot be given here.

The gelatin matrix itself has an important role in silver halide sensitivity. It forms an envelope around each crystal. It is adsorbed very intimately to the surface, and an electrical double layer, varying somewhat with the pH, exists at the crystal surface. Active gelatin contains sensitizing materials and permits diffusion of aqueous solutions through it so they can gain access to the surface of the grain. Gelatin itself is a buffer.

A number of phenomena describing the behavior of the latent image carry special names. For example, "solarization" is a phenomenon in which the developability of the latent image during a strong exposure ($10^4 \times$ threshold or more) regresses as the exposure continues. The grains are affected in some manner to resist development. This effect is a function of the development; silver halide solvent developers are little affected by solarization. Apparently only the external latent image is damaged. Emulsions rich in silver iodide have a higher tendency to solarize. It has been shown that the total amount of photolytic silver continues to increase as the exposure passes into the solarization region.

In the silver bromide polar bond a valence electron of silver is accepted by an adjacent bromine atom making a negative bromine ion. These electrons are the ones most easily raised to conduction bands in the crystal, so that absorption of light by the grain generally leads to the creation of a neutral bromine atom in the crystal. The atom may capture an electron from an adjacent bromine ion, thus effectively causing a bromine atom to diffuse through the emulsion. The process is termed "migration of positive holes." By it, bromine can go from the interior to the surface of a perfect microcrystal. If much photolysis takes place, the bromine released may become concentrated at the grain surface and the crystal environment must be a good halogen acceptor if the bromine is not to recombine with the free silver and destroy the surface latent image (that this actually happens is the best current explanation of solarization). By adding a nitrite to the emulsion, solarization can be avoided, and other reagents that combine readily with bromine can act similarly. It has been observed (Y 49) that reduction of the air pressure on photographic emulsion increases its sensitivity, possibly because the reduction in pressure also reduces the humidity, but also possibly because the removal of the bromine is facilitated. On bathing photographic emulsions with a dissolved halogen solution, even the internal latent image can be destroyed. This is taken as evidence that halogen atoms as positive holes can migrate with relative freedom through the silver halide lattice. The experimental facts on solarization at low temperatures are complicated by the low mobility of silver ions to form the latent image when the temperature is reduced, but none of the facts refute the rebromination theory of solarization.

Newly developed experimental techniques described by Hamilton (H 58) have enabled research workers of the Eastman Kodak Company to apply electric fields across silver halide crystals at the time they are exposed. The electrons then apparently migrate to the side having the higher electrostatic potential, and development begins only at latent image sites on this side of the crystal. It has been possible also to see the bromine diffuse into the gelatin and migrate in the expected direction counter to the electric field.

The "Herschel" effect is another well-known photographic phenomenon. This was originally observed to be a destruction of the latent image by red or infrared light of frequency below that necessary to produce a latent image. There is some evidence that moisture and/or oxygen complicate the effect. The explanation of the Herschel effect given by the Gurney-Mott theory (see Section 2.4) is that still generally held. Red or infrared light is absorbed by silver of the latent image, and electrons ejected go into the silver bromide conduction bands. The latent image becomes positively charged, and, especially when it consists of only a few atoms, is dispersed. It is found, however, that when a latent image speck is reduced in size by the Herschel effect, other specks may be formed or grow. Light of the wavelength used to produce the Herschel effect is not strongly absorbed in silver halide, so it penetrates the crystal and acts on the internal latent image as well as on the superficial silver. Because of the low absorption, however, between 10^6 and 10^9 times as much energy is required to disperse the image as it took to produce it. Experiments on the Herschel effect at low temperatures can be understood if the mobility of the silver ion is greatly reduced as the temperature falls. Intensification of the latent image by gold or mercury has been observed to stabilize the image so that it does not display the Herschel effect.

The Herschel effect should not, in fact, be considered as much an effect destroying the latent image as a means for redistributing it; under certain conditions the effect can be reversed. If the latent image is dispersed into many small silver specks, it may be undevelopable with developers of ordinary strength. With prolonged application of infrared light, however, the smaller specks may be destroyed, but if the wavelength is not too short, the larger ones can grow at their expense to developable dimensions.

The positive Herschel effect after treatment with chromic acid is called the "Debot" effect.

It is well known that very high *local* pressure on emulsion renders it developable, particularly if rubbing is also involved. Even drawing a fiber across an emulsion surface or sliding an emulsion surface on another smooth surface, if dust particles are between them, causes black lines, superficially resembling tracks, to become developable. Some of these effects probably are related to the well-known frictional, piezo-, or triboelectric effects, but their full analysis has not been published. Occasionally streaked blackening of the emulsion-glass surface of pellicles is observed and is attributed to a blackening by tension when the pellicle was peeled from the glass on which it was poured.

Two other photographic effects may have some importance for understanding the behavior of the latent image of particle tracks in emulsion. These are known as the "Clayden" effect and the "Albert" effect. The former is a desensitization of emulsion given a high intensity exposure of short duration followed by a weak exposure of longer duration. It was probably observed first in photographs of lightning strokes which appeared reversed. The Albert effect is a reversal observed when an emulsion is exposed, treated with chromic acid, and then given a second exposure and development.

An experimental fact of some significance is that visible photolytic silver appears internally along dislocations of large single crystals. Another is that flash illumination at high intensity produces a preponderance of "subimage" (see Section 2.4 for the theoretical interpretation of the subimage). These are among the phenomena that a satisfactory theory of the latent image must explain.

Berg (B 48) has described many other photographic effects, but in most cases they are not believed to be particularly relevant to the special problems of nuclear-track emulsion, and for their descriptions the reader is referred to his excellent review.

"Latensification" is a name for any one of several processes to intensify the latent image after exposure but before development. A complete understanding of the latent image presumably includes also an understanding of the means of latensification. The processes utilize various chemical agents such as mercury vapor, gold salts, hydrogen peroxide, or sulfur dioxide, as well as low intensity light. Generally speaking, latensification is most successful for short development times with weak developers, and for short exposures at high intensity. The effect of latensification decreases as the age of the latent image increases up to about 4 hr. The observations suggest that the latensification tends to convert a latent subimage into a stable latent image.

A procedure that may be useful for intensifying particle tracks in processed emulsion, and which even may bring back tracks apparently etched away completely by incorrect fixing is the following: a solution of 5 % $HgCl_3$ and 5 % KBr is prepared. The plates are presoaked in distilled water and then in the solution for about 10 min. Then it is developed in amidol developer diluted 10-100 times, fixed, washed, and dried. Concentrations of solutions may be altered for best results. The results of Yagoda (Y 49), however, show that sometimes attempted latensification by mercury vapor may damage the latent image, and the subject must be approached cautiously.

For a normal developer a latent subimage is characterized by a long induction period for development. The time can be reduced by the use of a strong developer. Postexposure may render such an image normally developable, but it is susceptible to partial destruction by the Herschel effect. This, however, also has a stabilizing effect on it because it redistributes the silver into more stable specks. The positive Herschel effect is well known to be more effective on an image produced by a short flash of high intensity than on the image produced by a prolonged low intensity irradiation.

Evans, Hedges, and Mitchell (EHM 55), by evaporating silver on clean silver bromide surfaces have simulated the presence of a surface subimage when less than 10^{14} atoms/cm^2 are present. More than 10^{15} atoms/cm^2 acts like a normally developable latent image.

The mode of formation and the behavior of the latent image at low temperatures is very important to the theory. Some systematic information is available for temperatures as low as that of liquid air, and a little work has been carried down to the liquid helium temperatures, but a definite need exists for more information in the region where the silver ions can have no mobility. It has been established that a low temperature after the latent image has formed, stabilizes and preserves it. Even plates exposed by lost arctic explorers many years ago still were developable when found recently because they had remained at a low temperature during the intervening time.

The effects of temperature on the emulsion sensitivity are complex. At very low temperatures silver ionic conduction ceases in the crystal so that a latent image cannot form until the temperature is raised. A latent preimage must be formed, however. Its stability doubtless is not high, and its survival is owing to the low temperature. It is possible that the sensitivity of a cold emulsion is affected by the temperature-time curve that it experiences in warming up. At a high temperature thermal agitation tends to destroy the latent image.

For these reasons, one might expect the sensitivity to pass through a maximum in the general vicinity of 0° C. In experiments at the Lawrence Radiation Laboratory with K.5 emulsion, R. Blinkenberg found a maximum of near-constant sensitivity from —20° to 20° C, with perhaps an indication of a dip near 0° C. Other observers have found multiple peaks. The Strasbourg data (R 58, D 58.1) for G. 5 emulsion using ID-19 developer imply that there are peaks at —40°, —15°, and 30° C, with dips between these temperatures. There is agreement that the sensitivity of G.5 emulsion falls at both high and low temperatures.

R. Rechenmann (R 58) has exposed dry emulsion at temperatures up to 100° C. It was found that, whereas the sensitivity of G.5 emulsion fell as the temperature rose, the C.2 emulsion increased in sensitivity. The fog did not increase with temperature and at 90° C with pyro development the ends of electron tracks were visible in C.2 emulsion.

Mme. M. Debeauvais-Wack (D 57) has studied the sensitivity of E.1, C.2, and G.5 nuclear-track emulsions exposed to light and particles at temperatures as low as —186° C. Using ID-19 developer, the tracks of alpha particles were visible only in G.5 emulsion when the temperature was —186° C, and the grain density was low. At —85° C alpha-particle tracks were visible in C.2 emulsion, and the tracks were continuous in G.5 emulsion.

When ordinary light was used to test emulsion sensitivity, it was found that whereas C.2 emulsion was more sensitive than G.5 emulsion at room temperature, as the temperature was reduced the G.5 became both relatively and absolutely more sensitive. On the other hand, for short exposures the sensitivity of G.5 emulsion also fell as the temperature was reduced.

Silver bromoiodide emulsions become fluorescent at about —170° C, and the fluorescence is accompanied by a considerable reduction of sensitivity. This further loss of sensitivity can probably be attributed to the energy lost by reradiation. Bogomolov, Rasorenova, and Sirotinskaya (BRS 57) have reduced the loss of sensitivity at low temperatures by eliminating iodine from the emulsion. Then the fluorescence occurs only weakly and at a very low temperature. With such an emulsion they retain a minimum grain density of 17 or 18 per 100 μ at the temperature of liquid hydrogen. They propose a mechanism by which the iodine in the crystal lattice at low temperatures causes the formation of shallow traps that facilitate the recapture of the conduction electrons by positive holes, with the liberation of the observed radiant energy.

The following is an account of experiments at the Massachusetts Institute of Technology given to the writer by Robert A. Schluter. G.5 emulsion was lowered to liquid hydrogen or liquid helium temperatures.

This emulsion was in the form of 100 μ pellicles stacked to a thickness of 1 cm. They were clamped between brass plates. The temperature of the lower plate was reduced first so that the temperature gradient was perpendicular to the pellicles. If this is not done the pellicles crack. The temperature was reduced during a period of 10 min, and was monitored by a thermocouple. The emulsion was protected from direct contact with the gas by a paper covering. After exposing the cold emulsion to the synchrotron γ-ray beam, it was warmed up quickly (in 15 min). The next day the emulsion was developed with Bristol developer (see Chapter 5) which contains sulfite, and is therefore a suitable developer for an internal latent image. The grain density of electrons in the emulsion was 22 per 100 μ as compared with 28 obtained with all the conditions the same except that the emulsion was not chilled.

The retention of this much sensitivity by G.5 emulsion has not generally been observed. Bogomolov *et al.* (BRRS 58), however, found on hypersensitizing iodide-free NIKFI type R emulsion with triethanolamine that they retained enough sensitivity at 20° K to record 76 grains per 100μ when the grain density was 87 per 100μ at ordinary temperatures.

The latent image of a particle track gradually fades after exposure so that if the emulsion is left unprocessed, the developed grain density will be smaller the longer the elapsed time between exposure and processing. This action is more rapid in emulsions of small grain size, and for emulsion kept at a high temperature and/or humidity. This effect is used to eradicate old tracks from the emulsion as described in Section 4.2. The stability of the latent image apparently depends at least partly on the sensitizing agent used in the manufacture of the emulsion. Gold is known to produce quite a stable image. Borax loading of the plates also reduces the fading because it raises the pH. Thin tracks fade relatively more rapidly than the tracks of heavily ionizing particles. The presence of oxidizing agents such as hydrogen peroxide or chromic acid greatly accelerates fading. Infrared radiation also affects the tracks because of the Herschel effect. The fading is more rapid in air or oxygen, especially near the surface of the emulsion, than in an atmosphere of nitrogen or in vacuum.* Because of the fading that takes place, emulsion should be developed soon after exposure and in the interim it should be kept cold and dry. It has been observed that considerable fading may take place between the time nuclear-track emulsion pellicles are wetted for mounting on glass, and the time when development is initiated. Emulsions flown in balloons to study cosmic radiation often suffer seriously from fading if they are exposed to hot weather and

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* Leide (L 62) minimizes the importance of this effect.

not recovered quickly. Ilford G.5 emulsion is remarkably resistant to fading, so with it the problem is usually not encountered in the acute form to be expected when finer grain emulsions are used, but serious loss of G.5 grain density has been reported when exposed emulsion is shipped and stored without refrigeration (K 54).

Some data on the fading of G.5 emulsion has been obtained by Barron and Wolfendale (BW 57). For a 50 % reduction in track density 1040 ± 200 days are required at 5° C, and 520 ± 50 days at 25° C. No difference was observed between storage in air or commercial argon. The normal fading mechanism in G.5 appears to be the thermal ejection of electrons from the latent image according to these authors.

A thorough study of fading in G.5 emulsion has been made by Leide (L 56). The emulsion was kept under a variety of carefully controlled humidity and temperature conditions, and tracks of various ages up to 99 days were compared photometrically. It was found that the fading near the surface was most pronounced, but this effect falls off rapidly with depth so that at 40 to 60 μ below the surface, the surface effect has vanished. In addition, a uniform fading that varies with the time, temperature, humidity, and "degree of development," takes place throughout the emulsion volume. The surface effect is attributed to oxygen from the atmosphere, but the volume effect seems to have a different origin.

The effect of fading on tracks, in the range of small to moderate fading, was found to be equivalent to a reduction of the rate of energy loss everywhere by a constant factor. While Ilford G.5 emulsion is very stable with respect to fading, in it the onset of fading as the temperature and/or humidity is raised above normal is sudden and remarkable. Whereas no fading was detected when 20° C storage was carried out for 2 months at 52 % relative humidity (R. H.), at the same temperature in plates kept at 75 % R.H. the apparent mass of a particle judged from the track-grain density was lowered to 0.54 of its true value. The effect of a 5° C rise in temperature, from 20° to 25° C at 75 % R.H. made the apparent mass drop to 0.05 of its true value. Storage even at 75 % R.H. produces no appreciable fading if the temperature is kept at 0° C.

Lohmann (L 56.1) investigated the fading in Agfa K-plates and came to essentially the same conclusion as Barron and Wolfendale on the mechanism of the fading.

The fading is expressed as a coefficient, $F = (N_0 - N)/N_0$, by Lanius (L 53), and in Agfa K-2 plates the magnitude of this coefficient is about 2.8×10^{-3} per day. In the definition of F, the quantity N_0 is the initial grain density while N is the grain density at a later time.

Albouy and Faraggi (AF 51) have carried out extensive studies of latent image fading with the following results: at constant humidity, the rate of fading increases exponentially with the absolute temperature, and at constant temperature the fading increases exponentially with the quantity of water retained by the gelatin. At constant temperature and humidity, the fading increases with increasing oxygen content of the gas in contact with the emulsion. The stability of the latent image is increased by added substances having a pH higher than that of the emulsion and is decreased by the addition of substances of lower pH. Fading occurs more rapidly the finer the grain size of the emulsion. They make the hypothesis that the latent image specks are oxidized by atmospheric oxygen under humid conditions, the oxidation proceeding more rapidly in acid conditions.

In recent experiments Leide (L 60) has studied the fading coefficient F for Ilford K.5 emulsion. He found $F = 0.25$ in 17 days at about 50 % relative humidity, at a temperature of 20° C on tracks of 185 Mev protons. His curves of F versus temperature and humidity definitely indicate that the latent image is more easily faded in K.5 emulsion than in G.5.

The fading of NIKFI type R emulsion has also been investigated by Bogomolov and Romanovskaya (BR 57). The ratio, F, was found to increase with time as expected. At the end of 36 days during which the emulsion was stored at 20° C and at a relative humidity of 58 %, a stack of normal emulsion gave a value of 0.2, while an experimental stack gave 0.5 for F. The results agreed with their theory of the fading, which assumed that the rate of fading varied inversely with the size of the latent image speck.

2.3 Development and Discrimination

Only a sketch of the general process of latent image development and related topics can be given here. An enormous literature of books, articles, and patents exists. Special development procedures that have been devised for nuclear-track emulsions will be treated further in Chapter 5.

A more exact understanding of the development processes is obtained by the quantitative methods of electrochemistry. This approach to emulsion making as well as to the development process is now being utilized widely. We shall first review some of the more pertinent facts and definitions.

A metal (specifically silver) in contact with a solution of its ions, has a tendency to detach electrons, viz., $Ag \rightarrow Ag^+ + e^-$, and this tendency can be measured. The single-electrode potential of the metal with respect to the solution is the usual measure of this propensity. It is not measured absolutely but relative to hydrogen. The concentration and activity coefficient of metal ions in solution affects the tendency for the solid metal to dissociate, and consequently it influences the measured potential. The potential difference E is related to the electrode-solution-system parameters by the equation:

$$E = E_0 - \left(\frac{RT}{F}\right) \ln \left[\frac{a_{\mathrm{H}^+} (a_{\mathrm{M}})^{1/n}}{(a_{\mathrm{H}_2})^{1/2} (a^{n+})^{1/n}}\right] \tag{2.3.1}$$

Here E_0 is the constant standard electrode potential; T is the absolute temperature; R is the gas constant per mole; F is the faraday; a_{H^+} is the activity of the hydrogen ion; a_{M} is the activity of the metal; n is the degree of ionization; a_{H_2} is the activity of gaseous hydrogen; and a^{n+} is the activity of the metal ion. Now the activity of pure, solid unstrained metal is defined to be unity, as are the activities of hydrogen gas at 1 atmosphere pressure and 1 mole of hydrogen ions per liter. The equation for pure unstrained metal relative to the normal hydrogen electrode then is

$$E = E_0 + \left(\frac{RT}{nF}\right) \ln (a_{\mathrm{M}^{n+}}) \tag{2.3.2}$$

The normal hydrogen electrode is prepared by absorbing pure hydrogen on platinum black. This electrode is not used much practically because the calomel electrodes are stabler and simpler to use. The potentials of mercurous chloride electrodes in various concentrations of potassium chloride are known accurately relative to the normal hydrogen electrode. For example, the normal calomel electrode (the calomel electrode in a normal potassium chloride solution) is 0.2805 volts positive with respect to the hydrogen electrode. The measured electrode potentials are 0.2805 volts lower when measured with respect to the normal calomel electrode than with respect to the normal hydrogen electrode.

The activity coefficients (the activities divided by the molar concentrations) normally rise toward unity as the concentration is decreased, and tables exist for the activity coefficients as functions of concentration. For example, at 25° C the activity coefficient of Ag^+ in a AgNO_3 solution is 0.95 at 10^{-3} M, 0.90 at 10^{-2} M, and 0.72 at 10^{-1} M.

With respect to either the calomel electrode or the hydrogen electrode, metals form an electromotive-force series such that each metal will displace from solution any other more electropositive than itself.

Hydrogen as a metal is in a special position; it is always present in water solutions and other potentials are measured with respect to the hydrogen potential. The hydrogen ion concentration is measured in gram ions per liter or by the pH. For example in a neutral solution the activity, $a_{H^+} = 10^{-7}$, and $pH = -\ln a_{H^+} = 7$. At 25° C the pH is found from

$$pH = \frac{(E - 0.2805)}{0.0591} \tag{2.3.3}$$

where E is measured with respect to the normal calomel electrode. Indicators of pH that change color at definite hydrogen ion concentrations may be used after calibration by electrode potential measurements.

For solutions more acid than pH 8, the quinhydrone electrode is a convenient substitute for the hydrogen electrode. At 25° C its value of E_0 is 0.6990 relative to the normal hydrogen electrode.

For alkaline solutions as well as in a wide variety of other applications for which neither calomel nor quinhydrone electrodes are suitable, the glass electrode is now being used for hydrogen ion concentration measurements. Activities or concentrations of ions other than hydrogen are sometimes measured by the negative logarithm of the ionic activity. Thus:

$$pAg = -\ln Ag^+ \tag{2.3.4}$$

When an electrode gives up electrons to the medium in which it is placed, its action is one of *reduction*; when it accepts electrons, its action is *oxidizing*. When ions in the medium exist in two different states of reduction their relative activities affect the electrode-solution potential difference, E:

$$E = E_0 - \frac{RT}{F} \ln \frac{a^{(n-1)+}}{a^{n+}} \tag{2.3.5}$$

E_0 is the potential that exists when the ions are equally active while $a^{(n-1)+}$ and a^{n+} are the relative activities (at low concentrations proportional to the concentrations) of the ions in the ionized states $(n-1)$ and n.

In titration, where equality of the ion concentrations is reached, E changes most rapidly for the addition of a given amount of reagent. While precipitation is occurring, the potential remains constant, and for a given ratio of ion concentrations E also remains constant. These facts are powerful aids in emulsion making and development, especially for experimental investigations of these processes.

In studying oxidation-reduction processes, it is usual to write Eq. (2.3.5) in the form (M 54):

$$E = E_0 - \frac{RT}{nF} \ln \frac{(\mathrm{OX})}{(\mathrm{Red})} \tag{2.3.6}$$

E is called the *redox* potential. Here (OX) and (Red) are approximately the respective concentrations of the oxidized and reduced forms of the reducing compound. When one ion is to be reduced by another, four concentrations are involved—the oxidized and reduced forms of each. Thus, if ferrous chloride is used to develop the latent image of silver, it is the difference of redox potentials in the oxidized and reduced forms of both that determine the resulting potential difference, ΔE.

$$\Delta E = E_{0\mathrm{Fe}^{3+},\mathrm{Fe}^{2+}} - E_{0\mathrm{Ag},\mathrm{Ag}^+} - \frac{RT}{F} \ln \frac{(\mathrm{Fe}^{3+})(\mathrm{Ag})}{(\mathrm{Fe}^{2+})(\mathrm{Ag}^+)} \tag{2.3.7}$$

The speed of development is governed by the magnitude of ΔE.

Dahl-Jensen (D 60) has tested several inorganic materials as developers for nuclear research emulsions. They included the ions Fe^{2+}, V^{3+}, Ti^{3+}, Cr^{3+} complexed with Versene acid. They are said to have both advantages and disadvantages for the development of thick pellicles.

For discussions of many of the numerous reducing agents that are used for development, the reader is referred to Mees (M 54). Broadly they are classified as inorganic agents containing metals of variable valence, inorganic nonmetallic agents, organic substitution products of inorganic developing agents, and organic developing agents. They can also be classified by their development rate or their reduction potential relative to a hydrogen electrode at a fixed pH. These classifications are useful but they do not fully describe the developers in their dependence on pH, their stability, their allergenic activity, and many other properties that have to be investigated separately.

Sulfites, bisulfites, or metabisulfites are almost universally included in the usual organic chemical developing solutions as preservatives because they prevent destruction of the developing agent by oxidation and thus also avoid gelatin stains from the developer oxidation products. In addition, sulfites have a solvent action on silver halide. An alkali or buffer usually is included in the developer to adjust the pH. Since developing agents increase in activity as the pH is raised these substances are known as "accelerators."

On the other hand, bromides are included as restrainers. They slow the development and are to some extent selective, slowing the development of fog more than the development of exposed grains.

Neutral salts such as sodium sulfate in a concentrated solution are effective in reducing gelatin swelling and are sometimes added for this purpose. Wetting agents are also sometimes included.

In describing their effects, developers are characterized by various adjectives as *surface* or *superficial* referring to developers that do not contain silver halide solvent and therefore can act only at the crystal surface in contrast to *solvent* developers. One may also refer to developers as *total* or *critical* (*tangent*) depending on how far the reduction potential of the developer exceeds the threshold for development. Since the threshold varies in some inverse manner with the size of the latent image speck, developers operating near threshold are *discriminating*.

Physical, as opposed to *chemical* developers, contain silver or perhaps other metal ions that deposit on the latent image centers.

The reduced silver resulting from chemical development is in the form of fine filaments. Under the electron microscope the grain has the appearance of a loose ball of yarn. Physically developed silver, however, is compact. Generally, several times as much exposure is required to develop a latent image by physical development alone. Presumably a larger, better coagulated latent image speck of photolytic silver is necessary for the initiation of physical development.

Physical development may cause the grains to grow enough during processing so that they crowd each other. The tracks of highly charged particles are especially subject to this effect. In Fig. 2.3.1 the buckled tracks of A^{40} are shown in the same field of view as a straight track of N^{14}. This development was with D 19 developer in the presence of uranium ions.

The developers in general use for nuclear research emulsions are combined chemical and physical developers. Sulfite and bromide are solvents of the silver halide. Complexes of silver halide form with these molecules. The silver ions in the complex are reduced to metallic silver which precipitates in the gelatin, and plates out on the silver grains. This causes physical development of the grains and dichroic fog. The size of the colloidal silver particles determines the color of the fog. Dense black layers of silver also can be formed by excess sulfite. These effects are aggravated by high pH and higher temperature. This fog is not to be confused with the fog grains that are similar in appearance to track grains and develop as a "single grain background" throughout the emulsion.

Successful development requires that the reaction in the grains containing the desired latent image proceed more rapidly than the development of the fog. The fog always limits the track-grain density obtainable merely by development. Prolonged action of a strong reducing agent develops all the silver halide microcrystals: The process is therefore one of discrimination by rate of reaction.

For nuclear-track emulsions, special kinds of discrimination are important. While not solely problems of development these are appropriate to introduce here.

Fig. 2.3.1. Buckled tracks of two A^{40} ions, and also the track of an N^{14} ion in G.5 emulsion. They show the effect of physical development on tracks of very highly ionizing particles. Argon ions in the buckled region suffer energy loss at a rate of about 5 Mev/μ. The nitrogen track is only slightly buckled although its rate of energy loss is about 1 Mev/μ. (Photomicrograph by C. Cole.)

A certain kind of discrimination is required for tracks of weakly-ionizing particles to be recognizable in the background fog of the emulsion. Another type is important for recognizing a specific type of track in the presence of numerous others.

By the discrimination of a nuclear-track emulsion one usually means the characteristic of the emulsion by which the tracks of particles ionizing differently are distinguishable.

Generally speaking, a wide range of ionization discrimination and high emulsion sensitivity are incompatible because the grain density in a track of a highly ionizing particle rapidly tends to saturate in a sensitive emulsion. If the emulsion is sensitive enough, every grain encountered by the ionizing particle may be rendered developable and discrimination is gone. The amount of information obtainable from an element of track can be increased and the range of grain sensitivities probably also can be improved by using grains of smaller size, a larger number of which will be traversed in a given path length. The reduction of grain size can be carried only to the point, however, where the developed grain still remains visible under an optical microscope. A great advance in discrimination was achieved by Demers (D 54) when he first showed that sensitivity to minimum tracks can be maintained while reducing the crystal size to 0.08 μ or less. Four or more separately resolved grains per micron can be counted in the developed track.

Recently Perfilov *et al.* (PNP 57) have reported a sensitive emulsion with very fine grains. Up to 60 developed grains per 100 μ in the tracks of particles at the minimum of ionization are obtained. Such fine-grain emulsions as the L-series manufactured by Ilford Ltd. also give excellent discrimination if plates having only as much sensitivity as necessary are selected, and if they are correctly developed.

By choice of an emulsion sensitivity appropriate to the rate of energy loss of the particles under study, much can be done to separate particle groups by appearance alone.

Rene and Vanderhaeghe (RV 58) have found an interesting way to increase the discrimination of coarse-grained emulsions, and at the same time to keep the emulsion sensitive to minimum ionizing particles. Ilford G.5 and G.0 are identical in composition, but G.5 is much more sensitive owing presumably to further sensitizing procedures. A thorough blend of equal parts of these emulsions was made, and found to have the expected behavior. The G.5 crystals remained sensitive to minimum tracks, but the tracks cannot easily be saturated because of the admixture of low-sensitivity crystals. A logarithmic type of response was obtained so that a broad range of ionization could be distinguished. Figure 2.3.2 is a π^- star in this type of emulsion.

In practice, often one may have no choice of an emulsion, or some special consideration is overriding. Then wise processing may remain the means available for obtaining discrimination. For resolving individual grains it is best to avoid developers such as D-19 which dissolve silver halide and bring about physical development by plating out silver on the developing grains. The grains then become large and cannot be separately resolved. The means available for effecting the discrimination are rather numerous. One may alter the type of developing agent, its concentration and time, as well as the pH and temperature of the solution. The bromide, sulfite, and silver ion content of the developer can also be changed. The emulsion can be subjected to a Herschel effect, or some other conditioning exposure. The latent image can be chemically bleached with chromic acid, hydrogen peroxide, or simply with moisture at an elevated temperature. On the other hand, latensification also can be employed to strengthen weak tracks.

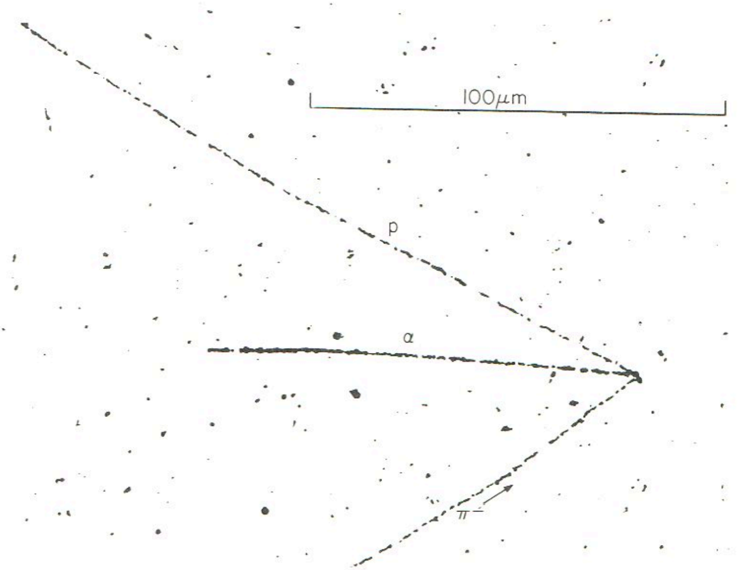

FIG. 2.3.2. Illustration of the effect of mixing emulsion crystals of two different sensitivities to achieve discrimination. (A mixture of $\frac{1}{2}$ G.5 and $\frac{1}{2}$ G.0 was used.) (Courtesy of G. Vanderhaeghe.)

Early work by Mortier and Vermaesen (MV 58) was directed toward obtaining discrimination between alpha-particle and proton tracks, and between alpha-particle and triton tracks. Gailloud and Haenny

(GH 52) also sought to obtain selective development of heavy particle tracks in gamma-ray fog. Considerable success was obtained in separating tracks of singly and doubly charged particles merely by varying the pH of development. Underdevelopment was also employed, and Gailloud and Haenny found glycine developer particularly useful. Detailed procedures and results of their work are given in their paper.

Bogomolov and Sirotinskaya (BS 57) have used a weak latent image solvent (sodium rhodanide is mentioned) for discriminating between tracks that ionize differently. By this means alpha particles and protons are separated and, by means of artificial fading, the tracks of fission fragments are retained while alpha-particle tracks are eradicated. Underdevelopment as employed in many earlier investigations was used by Bogomolov and Sirotinskaya to obtain practically complete discrimination between the alpha-triton disintegration tracks of Li^6 and protons recoiling from the fast neutron flux.

In Fig. 2.3.3 the discrimination between alpha particles and tritons obtained at Strasbourg is illustrated. Figure 2.3.4 shows the variety of appearances presented by alpha particles in the same emulsion when they are subjected to varying amounts of physical development.

Discriminating development was carried out by Cüer and Braun (CB 56) with critical developers adjusted in reduction potential to differentiate between tracks in which the latent images are differently dispersed. Because more than mere development, but "discriminatory development," is very important for nuclear-track emulsions, more will be said about this topic in later sections.

The following widely used equation describes reasonably well the developed density, D, of silver in an emulsion given an exposure E to light:

$$D = \gamma(\log E) + D_0 \tag{2.3.8}$$

The dependence on the exposure appears only in the log term. The quantity γ is an important measure of the development. It can be broken down into three terms as follows:

$$\gamma = A(\log t) + n\,\mathrm{pH} + G \tag{2.3.9}$$

Here t is the time of development (the equation is not valid for extremely long or short times). The constant A is characteristic of the developer. When γ is plotted against pH, two straight-line segments intersecting at about a pH of 9.7, and requiring different values of n and G for the different segments have been found. It is thought that some hydrolysis occurs at this point, and that this causes a change in the development

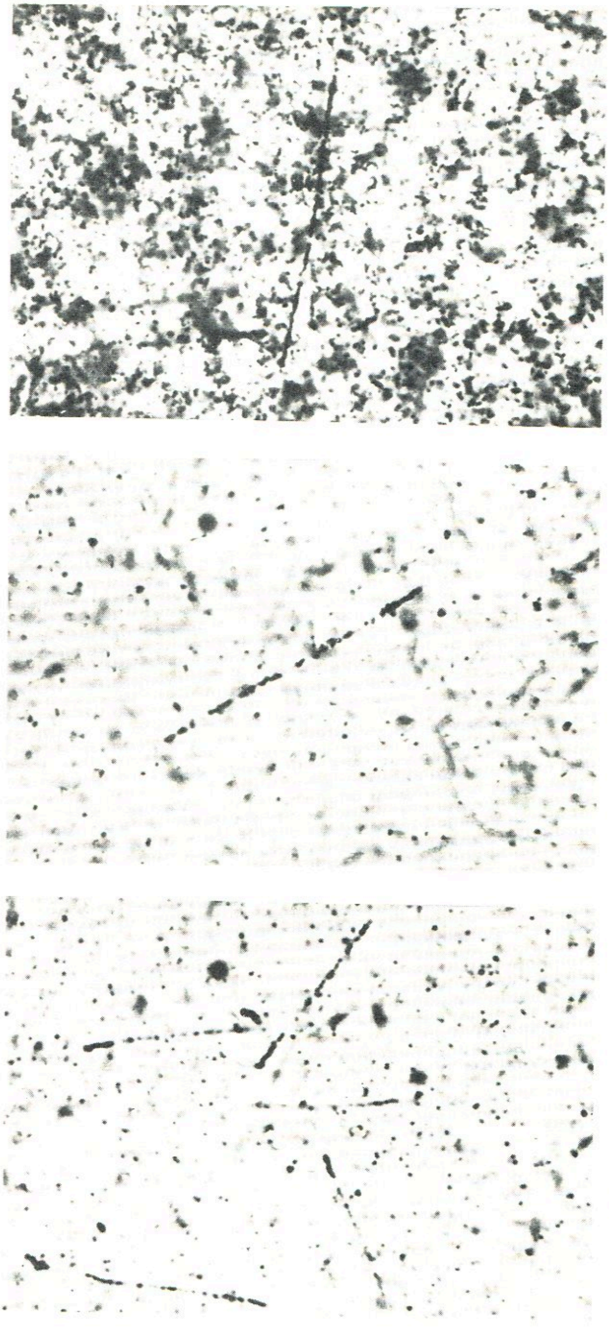

FIG. 2.3.3. The reaction $n + \mathrm{Li}^6 \rightarrow \mathrm{H}^3 + \mathrm{He}^4$ observed with varying discrimination between alpha particles, tritons, and electrons. (Courtesy of P. Cüer.)

behavior of the silver bromide. The values of n depend on the developer, and G depends on the type of emulsion. The quantity D_0 measures the pre-existing density, and that caused by fog. It depends on the development time according to the equation:

$$D_0 = C(\log t) + F \tag{2.3.10}$$

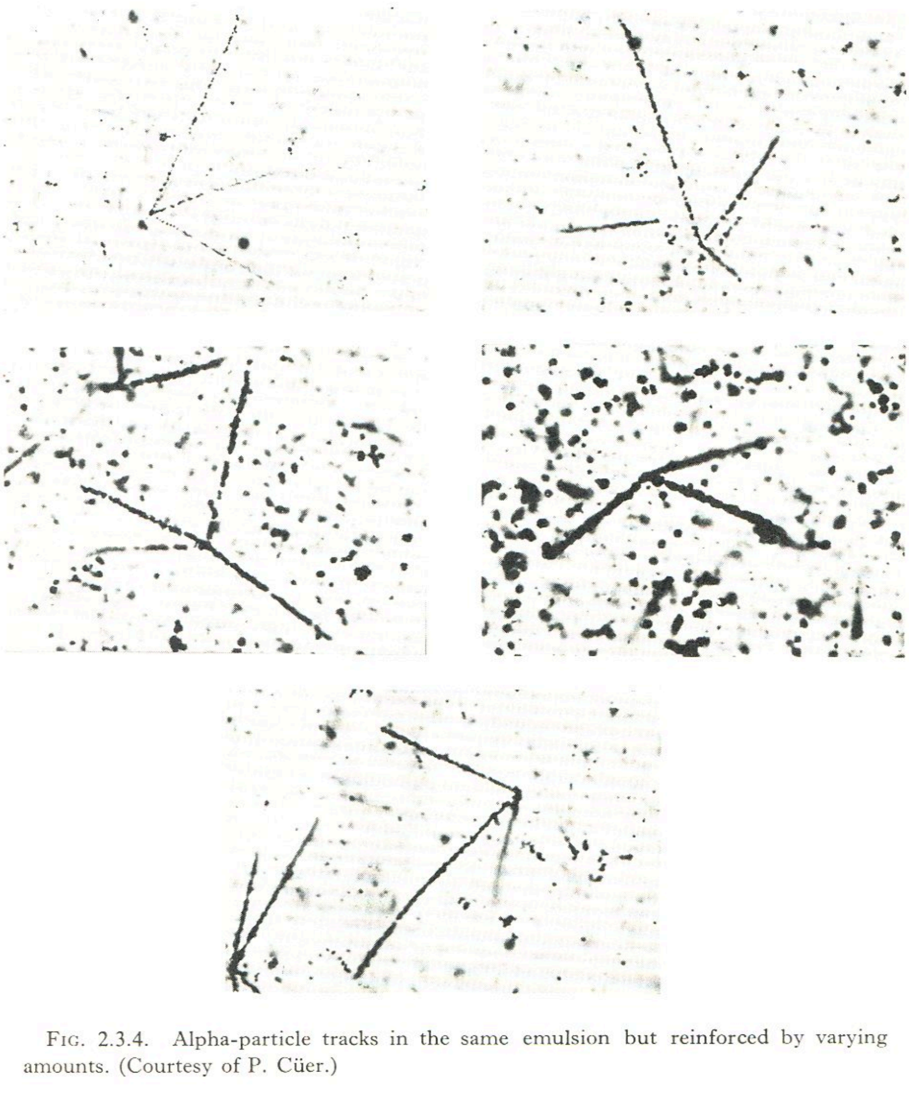

FIG. 2.3.4. Alpha-particle tracks in the same emulsion but reinforced by varying amounts. (Courtesy of P. Cüer.)

The rate of development, in common with that of most chemical reactions, varies rapidly with the temperature. In the small interval of temperatures ordinarily used for development, the relationship between the logarithm of the development time, t, and the centigrade temperature, T, is roughly linear:

$$\log t = -KT + Y \tag{2.3.11}$$

The temperature coefficient K varies in the approximate range 1.55-2.02, depending on the photographic material and the composition of the developer. For a particular pyrogallol developer containing potassium bromide, Mees (M 54) quotes results in which a constant temperature coefficient of 2.0 per degree centigrade was found for all emulsions tested. The temperature coefficient is also known sometimes to depend inversely on the pH value of the solution.

One can measure the capacity of a reducing solution to develop a latent image by the methods of electrochemistry as applied to oxidation-reduction systems. On measuring the electron-donating capacity of the reducing solution with respect to a standard electrode, it is found that 50-100 millivolts positive excess over the potential of a silver electrode is required before development actually proceeds. This is probably attributable to the small size and large relative surface area of the latent image specks. The potentials of pure reducing agents depend linearly on the pH of the system, increasing with increasing pH. The reducing potentials of many organic reducing agents are difficult to measure because the compounds are unstable, especially in the presence of oxygen.

The effect of alkali in developer, because of the constancy of the ion product, $[H^+]\,[OH^-]/H_2O$, is to lower the hydrogen ion concentration or to raise the pH. This, in turn, permits a larger concentration of the active anion that brings about the development. All the usual developing agents increase rapidly in activity as the pH is raised.

The developer is unstable, however, unless the pH is controlled by a buffer in the developing solution, and some agents are suitable for developers only in a very limited pH range.

The effect of sulfite in developer, which tends to prevent oxidation of the developing agent by dissolved oxygen from the air, often changes the speed of the development. The presence of the oxidation products of many developers increases the development rate of the solution, while other oxidation products may slow it. A second reason why sulfite affects the development rate is that it is a silver bromide solvent and, therefore, while exposing the internal latent image to the developing agent, may also dissolve away an excessive amount of halide.

Whether the form used is sodium sulfite or sodium bisulfite also affects the development rate.

Because of the common ion effect, the presence of a soluble bromide in the developing solution lowers the silver ion concentration, and restrains the development rate. This effect is discriminatory, and generally inhibits the growth of fog more than the development of the latent image. It is particularly important that bromide be used in processing nuclear-track emulsion when using the immersed hot stage (see Section 5.5), or fog will develop in the upper emulsion layers. Too much KBr has a deleterious effect because then the silver ion concentration can be driven so low that metallic silver goes into solution, perhaps destroying the latent image.

For an inorganic developer such as ferrooxalate the development rate generally is proportional to the concentration of the developing agent. This is not as good a rule for organic developers, and the γ to which the development is carried for a fixed product of concentration and development time varies somewhat with concentration. The value of γ usually passes through a maximum as the concentration is varied. For amidol this concentration is about 5 gm/liter at 15° C. It makes a difference, also, whether the developing agent alone or the developing solution concentration is changed, particularly because the pH may not remain constant.

Absorption probably plays a part in the development rates of such a developing agent as hydroquinone. James (J 40) found that the development rate of sulfite-free hydroquinone varied with the square root of the hydroquinone concentration and linearly with the hydroxyl ion concentration.

2.4 Recent Theory of the Latent Image

Much of modern thought on the photographic process stems from ideas developed by Gurney and Mott (GM 38) who proposed a theory of silver halide sensitivity in 1938. For the first time quantum mechanics and the then available solid-state theory were applied to this problem. At that date, of course, there was available an immense amount of empirical information and many theories of silver halide sensitivity had already been proposed. It does not seem important to recall them now, although a number of features of the Gurney-Mott theory had been introduced earlier. As their most important contribution Gurney and Mott adduced the idea that both electronic and ionic conduction play a part in the production of the latent image. This is called by Mitchell

(M 58.1) the Gurney-Mott principle. It remains a part of current thought about the process of forming the latent image. Gurney and Mott proposed specifically that photons are absorbed in silver halide to produce electrons in conduction bands and positive holes (halogen atoms). The electrons move freely until they encounter a local potential energy minimum where they can be trapped. Colloidal silver and "sensitivity specks", believed by Sheppard (S 25) to be silver sulfide, were conceived to be such traps. After capturing electrons the traps, being then negatively charged, would attract interstitial silver ions (Frenkel defects) to the trap sites, and particles of silver could be formed. This mechanism for producing the print-out effect is still believed to operate once many atoms of silver have formed a stable latent image. The migration of silver from surface kink sites to the surface latent image also can proceed with low activation energy and this process is supposed by J. W. Mitchell (M 58.1) to take place.

The initial stages of the formation of the latent image have been discussed in detail by Mitchell in a number of papers, an important one of which was written in collaboration with N. F. Mott (MM 57). He has evolved a model for the events leading up to the formation of a stable image quite at variance with that of Gurney and Mott.

He points out that the Gurney-Mott theory provided no process for the formation of internal latent image and made no reference to crystal imperfections. He also asks why the recombination of the charge carriers should not be more probable than trapping processes leading to photochemical changes. In addition he believes that it is not possible for uncharged centers such as small groups of silver atoms or of molecules of silver sulfide to provide stable traps for conduction electrons at room temperatures, as postulated in the Gurney-Mott theory. Regarding development, he states that it is not possible to explain the initiation of development by a latent subimage on the basis of the Gurney-Mott theory of development because, in the aqueous system, a pair of silver atoms can scarcely provide a stable trap for an electron from a reducing molecule. One of Mitchell's theses is that the mobility of the positive holes, neglected in the theory of Gurney and Mott, is large enough so that at room temperature they can migrate to surface traps and escape as free halide. The recombination of the electrons and positive holes, which otherwise would be logically demanded, is thereby averted. Positive holes are not attracted to metallic silver because in the silver halide crystal, silver has a positive potential.

The latent image, in Mitchell's theory, starts with a "preimage speck" consisting of a silver ion held to a silver-terminated kink site by an electron. The mean life of this configuration is estimated to be 10^{-5}

to 1 sec. The addition of a second interstitial silver ion and another photoelectron is the next stage in the process of forming the latent image. This is called the "subimage," and consists of Ag_2 absorbed at a kink site. A stable latent image is achieved when two more interstitial silver ions and a further electron are added. Not less than 3 silver atoms adsorbed to the silver bromide surface are necessary for stability, and 4 is the minimum number that will remain normally with a positive charge.

The role of sulfur in this theory is to prevent positive holes from oxidizing surface silver. When the sulfur is used up, solarization occurs. The presence of Ag_2S on the crystal surface also has been shown to stabilize silver atoms there, and those formed photolytically will not diffuse into the interior. According to Mitchell and Mott there is no evidence for the assumption that silver sulfide traps electrons. Evidence cited against this assumption is that similar emulsions with and without sulfur sensitization have practically identical amounts of internal latent image, while the surface latent image is absent from the unsensitized crystals. Without sulfur, the external latent image is rebrominated by the positive holes which diffuse to the surface.

The explanation of reciprocity failure on Mitchell's theory may be summarized as follows: at low intensities of irradiation even the slow recombination of electrons with positive holes becomes destructive because two electrons are necessary to form a latent subimage, and if a second electron does not arrive before the first is lost no subimage is formed. Very high intensity for a short time of irradiation, equivalent to the passage of a fast charged particle through the crystal, causes failure in another way. Mitchell believes that many electron-ion pairs will then find adsorbed silver atoms with which to combine before the ion and electron dissociate, and that many of these again will find silver ions with which to combine to form Ag_3^+, but, if the duration of the exposure is very short, by that time there will be no free electrons left to produce stable Ag_3.

Mitchell and his collaborators have found that iodide in the crystals has the effect of producing strains and concentration gradients so that dislocations are produced. A main role of iodide, therefore, is probably to introduce crystal imperfections.

Development takes place when the reduction potential of the developer is high enough so that the developer can donate electrons to the silver. Silver ions will then migrate to the silver and deposit on it. Whether the silver forms filaments or spongy masses, according to Mitchell and Mott, depends on the developer potential. If it is high enough to keep the silver negative, silver ions will be attracted to the ends of filaments where the field is high; otherwise no filaments are formed.

They account for a long induction period in the development of a latent subimage by pointing out that a three-body collision of latent subimage, silver ion, and developer molecule is necessary to initiate development in this situation. Introduction of gold atoms may reduce the induction period because a latent subimage containing a gold atom probably is more effective in holding a third atom.

Professor Hautot and his collaborators at Liege (HS 57, S 57, H 57) have carried out a number of investigations, the interpretation of which leads them to some conclusions at variance with those of Mitchell. Their experiments usually start with the fine-grain *primitive* emulsion mentioned in Chapter 1. The gelatin is inactive, and does not complicate their controlled sensitization of the halide crystals. The labile sulfur content of such an emulsion is less than 2×10^{-6} gm per gram of AgBr. No gelatin is, however, completely inert, especially when large, well-ripened grains are prepared. Some of their experiments are as follows:

To the primitive emulsion sensitizing solutions are added: $AuCl_4H$, $Au(CNS)_2K$, active gelatine, sodium thiosulfate, stannous chloride, organic reducing agents, etc. Development is carried out both with superficial and internal developers. For the first time by experiment Hautot has shown that the specks at the latent image sites do not have the same chemical nature when the emulsion is sensitized in different ways. Chromic acid in varying concentrations is used to bathe the emulsion, and the concentration required to destroy the latent image is observed. It was found that the latent image in primitive emulsion or in emulsion sensitized with organic or mineral reducers was easily destroyed by chromic acid, that in sulfur-sensitized emulsion the latent image was more resistant, and in gold-sensitized emulsion the latent image was difficult to destroy. It was found also that the maximum sensitivity increased with increasing quantities of sulfur and most other sensitizers, but eventually the increase in the fog prevented further sensitization in this way. Gold sensitization, however, behaved differently. The sensitivity passed through a maximum and then decreased as the quantity of added dithiocyanate aurate of potassium was gradually raised. It was found also that in unsensitized emulsions there was severe reciprocity failure with weak light intensities, but that sulfur sensitization, and especially gold sensitization, greatly reduced this effect. Another result of the work at Liege is to show that in sulfur-sensitized emulsions the importance of the internal latent image generally is decreased by the sensitization when the emulsion is subjected to a prolonged maturation.

It is concluded that sensitization makes a difference in the nature of the latent image specks because the resistance to oxidation is different with different agents. It is also concluded that the latent image specks in primitive emulsions and in reducer-sensitized emulsions are the same—probably silver. Primitive sensitivity is attributed to imperfections in the crystal. During ripening, sulfur is supposed to collect on the crystal from gelatin containing labile sulfur, and sulfur sensitized emulsions are believed by Liege school to contain latent image sites with sulfur replacing bromine. Gold-sensitized emulsion is considered to have latent image sites containing gold atoms. These beliefs are confirmed by using the Herschel effect and observing the relative difficulty with which latent images are dispersed by exposure to near infrared light.

Hautot and Sauvenier (HS 57) believe that the function of the sulfur-sensitizing agents is to produce colloidal specks on the surface of the microcrystalline grain, while the Bristol workers suggest that they are merely adsorbed to the crystals and serve chiefly as traps for positive holes.

C. S. Bogomolov (B 57) has made some interesting new theoretical and experimental contributions to the problem of the sensitivity of silver halide crystals to ionizing particles. His experiments led him to believe that only the ionization in a thin surface layer, the thickness of which he deduces to be $0.078 \pm 0.01\ \mu$, contributes to the developable latent image on the surface of the crystal. Therefore, instead of a mean effective path length in a spherical crystal of $(4/3)R$, the mean path is $4b\ [1 - (b/R) + b^2/3R^2]$, where R is the crystal radius and b is the thickness of the effective layer.

He also develops the point, stressed by the writer at the "Colloque de photographie" (Paris, September 24-29, 1951), that the mean energy loss in an emulsion crystal calculated from the Bethe-Bloch theory (See Chapter 9) is not appropriate for determining its developability. Extremely large fluctuations from the average energy loss occur in short segments of path.

Bogomolov postulates that in a given crystal path the number of effective ionizing acts is described by a Poisson distribution. His theory (B 57) of the grain density in tracks of weakly ionizing particles makes explicit use of the proposition that the grain sensitivity is confined to a surface layer. Experiments which were the basis for this hypothesis were carried out by Bogomolov and his collaborators.

They established that blackening produced in a series of nuclear research emulsions by electrons in the 20-90 Kev range is proportional to the grain diameter, other factors being held constant. In other words, the probability of development of a grain in the emulsions after being traversed by a charged particle is independent of its size. This observation was published by Bogomolov *et al.* (BDZ 56), who concluded that only energy losses in a thin layer of the surface are photographically effective.

Further experiments (BDMS 56) employed the K_α X-rays of copper, chromium, and cobalt. Then the electrons ejected by the photoelectric effect in the L-shells of Ag and Br had ranges small compared to the grain radius. In highly sensitized emulsions they found quantum yields (developed grains per photon absorbed in AgBr) of typically 0.25-0.5. This experiment confirmed their previous results.

Other experimental results by leading investigators suggest that the theory of the latent image, especially with regard to its behavior at low temperatures and in its interpretation of the role of impurities may still not be in its final form. In support of this point of view one may cite researches at Strasbourg carried on by Professor P. Cüer and his collaborators.

P. Cüer and his co-workers (C 57, CS 56, B 57.1, SS 57, CGL 56, D 57, CB 56) have stressed the importance of the condition of dispersion of the latent image in interpreting its behavior. In terms of this concept they are able to account for quite diverse experimental results in which, for example, the nature of the radiation causing the latent image is varied; the image is exposed to post illumination by infrared radiation; the character of the developer is changed; or the temperature is greatly reduced. The crystals of such an emulsion as Ilford G.5 (in contrast to C.2) are supposed to contain many possible surface latent image sites. On exposure to radiation of short duration or at a low temperature the image is conceived to be dispersed, that is, the latent image germs, while perhaps numerous, are all small. Under these conditions development proceeds with a large induction period even when the developer is strong, and with a tangent developer, great discrimination in the developability of latent images of differing degrees of dispersion is achieved.

In G.5 emulsion, superficial and solvent developers do not perform differently, leading them to the conclusion that the internal latent image here is unimportant.

In studying reciprocity using ordinary light in the region of no failure, both C.2 and D.1 emulsion are as sensitive as G.5, and for low intensity light they become relatively more sensitive. On the other hand for exposures of 10^{-6} sec, G.5 is more sensitive. On reducing the temperature, in contrast to the other emulsions, G.5 increases in sensitivity to light when a total developer is used.

The positive Herschel effect has been studied in nuclear track emulsion (SMB 51, CS 53). At Strasbourg irradiation in the wavelength interval 0.7 to 0.9 μ has proved to be useful for obtaining discrimination.

Strong latent image specks, consisting of many atoms of silver, require for dispersal more energy than that provided by photons of 0.7 μ wavelength, whereas small specks can be dispersed with quanta of this energy. The silver released on destruction of weak images migrates to larger silver aggregates, thus further strengthening them. Employment of a critical developer enhances the discrimination still more. A substantial gain was observed in this way when Professor Cüer and his collaborators studied alpha-particle and proton tracks in the presence of gamma radiation. Typical conditions for the Herschel exposure that have been used at Strasbourg are as follows: the lamp producing the infrared light was a 375 watt infrared lamp. Thin layers of emulsion were exposed at a distance of 10 cm through a filter that cuts off almost completely at 7000 A and absolutely at 6440 A. The times of exposure were 3 min for C.2 and 10 min for G.5 emulsion. Fog developed in C.2 from the tail of the spectral distribution when a longer exposure time was tried.

A developer found suitable for heightening the discrimination obtained with the Herschel effect is the following: a buffer of 12.4 gm of boric acid and 4 gm of sodium hydroxide per liter is prepared. Then 138 ml of buffer and 112 ml of 0.1 *N.* NaOH are added to 1.4 gm of hydroquinone and 1.5 gm of KBr. The pH should be 10.2. This developer contains no sulfite and "oxidizes very rapidly."

The latent image produced at a low temperature and which has been given no postexposure is developed only weakly by such a critical developer.

The results obtained using this method have been spectacular but as yet not very reproducible. Some tests have been made in which proton tracks could be found in a background of up to 30,000 r of gamma radiation. Recent research has been devoted to obtaining more reproducible results. By largely eliminating oxygen, some reduction in the oxidation rate of hydroquinone was achieved, but its reduction potential did not yet attain a well-determined value, probably because of the presence of varying concentrations of oxidation products.

Promising results have been obtained by Braun (B 57.1) using an inorganic potassium ferrooxalate developer prepared from three stable stock solutions that has a reproducible reduction potential, that penetrates gelatin rapidly, that operates through a range of pH, that has no complicated products of oxidation, and has other desirable properties. Braun has measured the reduction potential required to develop alpha-particle tracks in C.2 in 30 min with this developer at 18° C. The work was done as a function of KBr concentration for ordinary emulsion as well as some that had received a postexposure to infrared light. The values measured for the postexposed emulsion were found to be consistently 6 to 10 mv more positive (less reducing) than those found for unexposed emulsion. It was found that reducing potentials about 10 mv higher were required to develop the grains produced by beta and gamma radiation in 30 min at 18° C. It is also interesting that G.5 emulsion images required reducing potentials about 35 mv higher than C.2 emulsion for development under the same conditions. This effect is explained by Cüer by assuming that the latent image specks in G.5 are smaller but more numerous than those in C.2.

Using the ferrooxalate developer Braun (B58.1) has sought the conditions for optimum discrimination, and has been able to discern alpha-particle tracks in a gamma ray intensity of 4000 r. This result was reproducible.

Physical development has been used by Cüer, Gegauff, and Lonchamp (CGL 56) to obtain enhanced discrimination between the tracks of heavy particles and gamma-ray-produced electron tracks. The emulsion was first given a period of chemical development to enlarge the silver specks in the crystals that already had well-developed photolytic latent images, but short enough not to extend beyond the induction period for weak images. Then it was washed for 12 hr and developed for 90 to 180 min in a freshly prepared physical developer that contained equal parts of hydroquinone and quinone and in which the pH was adjusted so that the oxidation-reduction potential relative to the normal hydrogen electrode was 560 mv. The emulsion was then fixed. Fixing is also sometimes carried out before the physical development. The results of the treatment described were better when C.2 emulsion was used than when G.5 was tried. Thick emulsions were not successfully treated, but emulsions up to 100 μ in thickness were processed. The chemical development was carried out by presoaking the emulsion in cold developer and then raising the temperature, in the manner usual for thick emulsions (Chapter 5).

In Fig. 2.3.3 is shown the effect obtainable by this method. While good discrimination against gamma-ray background is obtained, and alpha-particle and proton tracks can usually be distinguished from each other, the discrimination against gamma radiation is not as striking as that obtained by Cüer and Braun (CB 56) when they used the Herschel effect in conjunction with critical development, followed by image intensification.

Schmitt and Simon (SS 57) have found that emulsions G.5 and NT-4 that are sensitive to minimum ionizing tracks do not exhibit high intensity reciprocity failure when exposed to light flashes of varying duration. K.0 emulsion also behaves in this way. The gamma of the development of G.5 emulsion was found to increase continuously as the exposure time was decreased. They also observe that the latent image germs produced by light flashes of varied duration in C.2 emulsion differ little among themselves whereas for G.5 and K.0 emulsions the differences were notable. In other experiments they have studied the number of grains carrying a latent image exceeding a certain critical size as judged by the developed density (using a nonsolvent pyrocatechine developer) relative to a standard density produced in the same emulsion by ID-19 developer. With increasing exposure time the observed density ratio rose for all emulsions, but, whereas the curve flattened off for all nuclear-track emulsions, the density ratio continued to rise beyond exposure times of 7 min for Kodak "Kodaline" film. The rise in density of C.2 emulsion was least marked.

The age of the emulsion was observed to affect its latent image behavior in such a way as to reduce the reciprocity failure for long exposures, and in other ways that are explainable by supposing that with time the sensitivity centers "coagulate" and their number diminishes.

The behavior of nuclear-track emulsions on exposure to light permit Schmitt and Simon to arrive at some additional conclusions. The relative sensitivity to light flashes of short duration (say 10^{-6} sec) measures the relative sensitivities of various emulsions to particles. The gamma of the development is an index of the discrimination. A high gamma indicates good discrimination in a limited interval corresponding to the steep part of the density versus log exposure curve. On the other hand if the gamma is low there is a wide interval of energy loss rates in which some discrimination is possible. From the work of Professor Cüer's group one arrives at certain generalizations. (*a*) Different types of radiation and conditions of irradiation lead to quite different distributions of numbers and sizes of silver latent image specks disposed for the most part on the surface of the silver halide crystal. (*b*) The developability of various sizes of latent image specks can be selective by control of the developer potential and by the judicious use of physical development. (*c*) The Herschel effect can be employed selectively to increase the discrimination by redistributing the image. (*d*) By the use of nonsolvent critical developers, only crystals with strong surface latent images need be developed. (*e*) By the use of "tangent" developers having critical reduction potentials and pH values, one can be selective in the size of the latent image speck that is developed. (*f*) By the use of post-intensification with mercury further discriminative control can be exercised.

Some recent important investigations have centered about the hypersensitizing action of triethanolamine (TEA). It seems to differ rather fundamentally from that of other sensitizers. On washing an emulsion containing TEA, for example, the effect is lost. On the other hand, mere washing of untreated emulsion does not spoil its sensitivity. The action of TEA is more marked when it is introduced into the plate by soaking in a TEA solution than when it is incorporated into the liquid emulsion. A side effect of TEA is to raise the pH, which raises the sensitivity and the fog together. The phenomenon under discussion, however, is an additional sensitization. Bogomolov *et al.* (B-D 58) seemed to have demonstrated, in well-conceived experiments, that energy absorbed by gelatin containing TEA is utilized in creating the latent image.

In subsequent experiments (BRS 60), however, they could not measure an increase in the emulsion photoconductivity due to hypersensitization. For this reason they have been forced to abandon the hypothesis that energy absorbed in the gelatin is transferred to the halide. TEA has no sensitizing action in neutral or acid media.

Frieser, Heimann, and Ranz (FHR 60) performed experiments which led them to conclude that TEA has no sensitizing effect due to halogen acceptance. They repeated the experiments of Bogomolov *et al.* (B-D 58) using electron bombardment. They found that on varying the thickness of a gelatin layer covering the emulsion, the ratio of sensitivities of hypersensitized to untreated emulsion went through a maximum for a thickness of 5 μ, but the effect was smaller than that reported by Bogomolov. The effect of TEA, according to Frieser *et al.* is rather complex and may be explained by the cooperation of different properties which are all working in the same sense.

A part of the effect is thought to arise from a combination of the hydroxyl ions with gelatin which reduces the pAg. The silver halide dissolving action of TEA also plays a part. An $[Ag(TEA)_2]^+$-complex is formed, but it is unstable and decays, reducing Ag^+ to silver.

The "supersensitizing" effect of combinations of dyes or other compounds adsorbed to the crystal has been discussed by Mees (M 54). It may be a relevant phenomenon here.

CHAPTER 3

Physical and Chemical Constitution of Nuclear-Track Emulsions

3.1 General Description

Emulsions used for the recording of charged particle tracks consist of an inorganic component, silver halide microcrystals, and usually about an equal volume of "gel phase," consisting mainly of gelatin with a variable quantity of water and small amounts of glycerol, sensitizer, and possibly other substances. The equilibrium water content depends on the relative humidity and temperature of the air in contact with the emulsion.

The silver halide is usually in the form of silver bromide crystals with a small amount of iodine in the crystal lattice, but other types of silver halide emulsions have been used, e.g. Demers' (D 58). There have also been attempts to replace the gelatin matrix of the emulsion by synthetic materials, but thus far without complete success.

3.2 The Silver Halide Microcrystals

Under the electron microscope the size and shape of the silver halide crystals can be observed. The diameter distributions as well as the shapes of the crystals in three emulsions of identical chemical composition can be studied in Fig. 3.2.1. The density of the silver halide is generally assumed not to depend on the crystal size, and 6.473 gm/ml is the accepted value. In such very small volumes, however, this presumption may not be justified. Occhialini (O 57) raised the question whether there might not be occluded water in the crystal structure. Cüer (C 57), on the other hand, has found no evidence for an internal latent image in the very small crystals of nuclear-track emulsion, and attributes this fact to a perfect crystal structure that would provide no internal latent image sites.

In Table 1.3.1 mean crystal-grain diameters are given for a number of emulsions. The grains in any particular emulsion sample are not all

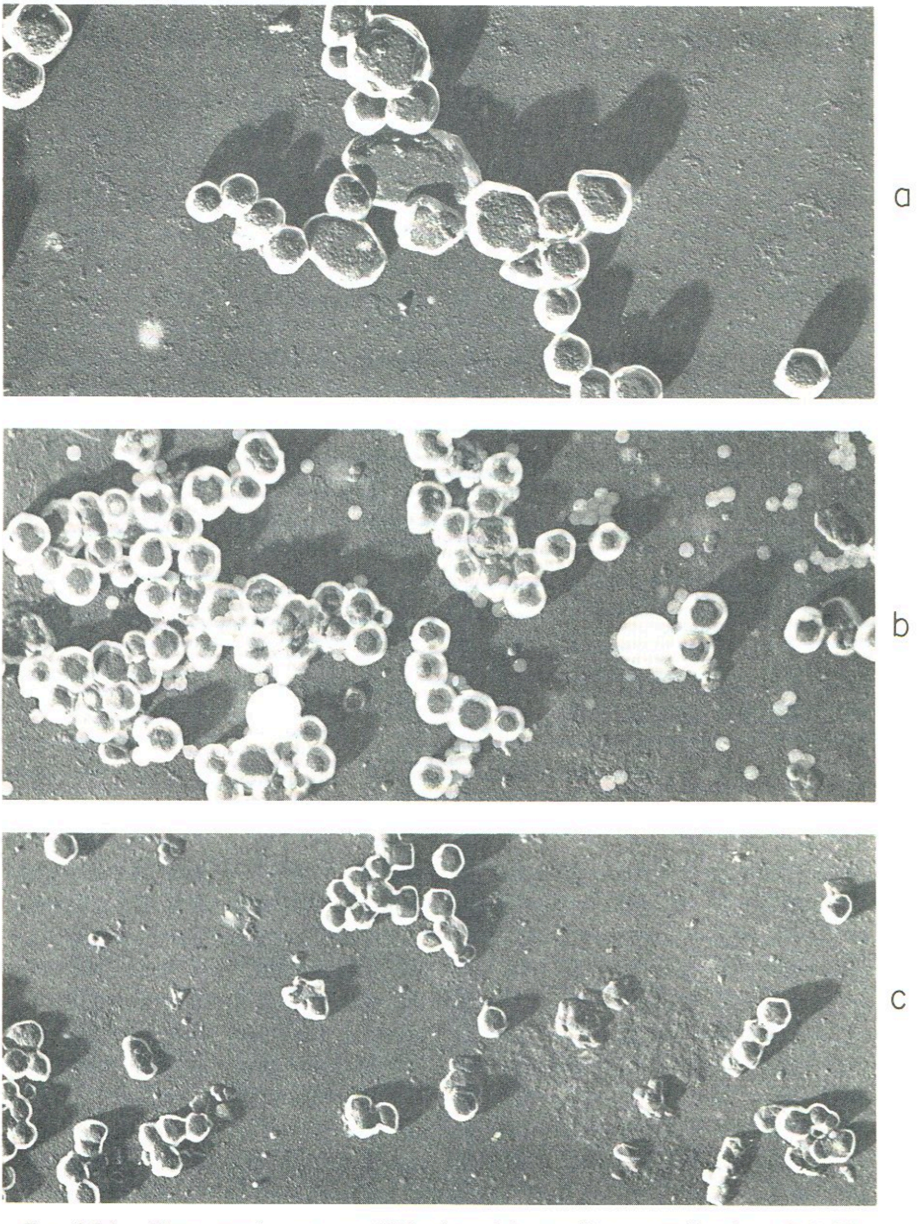

FIG. 3.2.1. Electron micrograms of Ilford emulsions with a magnification of 13,200 (*a*) G.5 emulsion; (*b*) K.5 emulsion; and (*c*) L.4 emulsion. (Carbon replica—shadowed with gold/palladium. Courtesy Ilford Ltd.)

of the same size, however, but are distributed with a certain variance of diameter. Kumar (K 58.1) found that the diameter of L.4 emulsion grains had a mean value of 0.134 μ with a standard deviation of 0.004 μ. Those of K.5 emulsion had a mean of 0.210 μ and a standard deviation of 0.007 μ (see Fig. 3.2.2). Numerous other measurements of grain diameters have been made.

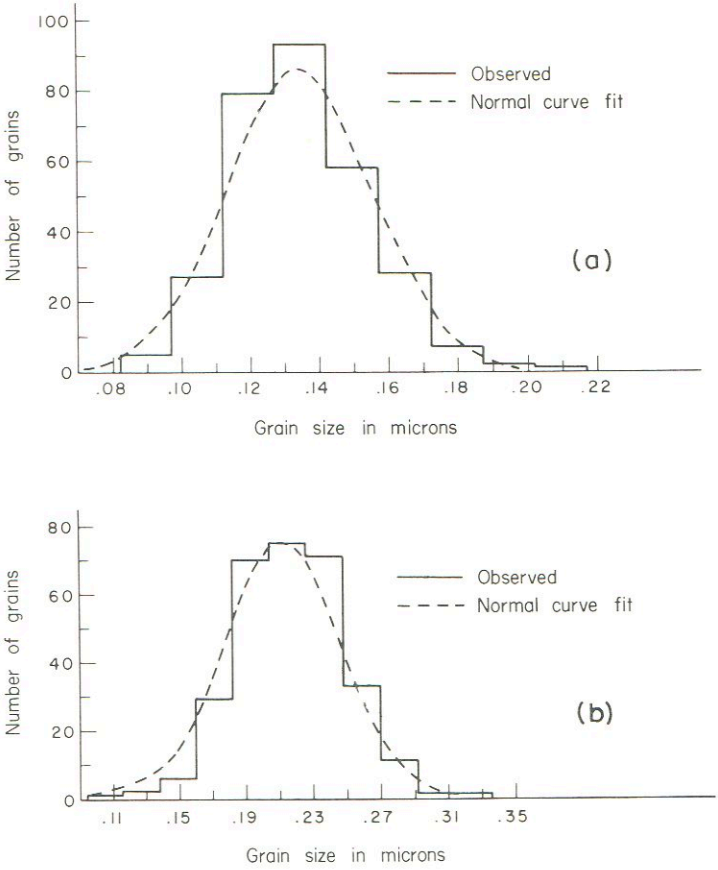

FIG. 3.2.2. (*a*) The observed grain-size distribution of Ilford L.4 emulsion. (*b*) The observed grain-size distribution of Ilford K.5 emulsion. (Courtesy of R. C. Kumar.)

The distribution of grain diameters in Ilford G.5 emulsion was determined by the writer in an electron microscope study, and the characteristics of the grain-size distribution are as follows:

Mean diameter, $\langle D\rangle = 0.275\ \mu$

Variance of diameter, $\sigma^2 = 0.0022\ \mu^2$

Asymmetry of distribution, $\langle(D - \langle D\rangle)^3\rangle = -1.7 \times 10^{-5}\ \mu^3$

Perfilov, Novikova, and Prokofyeva (PNP 57) have compared their emulsion PR with G.5 emulsion, and from their curves one obtains 0.08 μ and 0.32 μ for the respective modal diameters. For each distribution the standard deviation is about 20 % of the mode, in reasonable agreement with the writer's observations on G.5 emulsion. Most other studies of the grain sizes are in general agreement with the figures quoted.

Generally the contrast of a photographic emulsion is improved if the grains are made of a uniform size, and as a rule, the sensitivity goes up with increasing grain size. In a mixture of grain sizes, too, the larger crystals tend to have a greater proportion of the iodide. Mixed crystals of silver bromide and silver iodide do not generally form for all proportions of the halides, but when the iodine content is small, they do.

Bogomolov *et al.* (BSDU 57) ascribe an improved uniformity of grain size obtained in their emulsions to lamellar separation of the emulsion. Improved uniformity of grain size is also obtainable by arranging for uniform conditions of precipitation and ripening for all parts of the emulsion batch. Often the gelatin/silver/halide ratios are different or less well controlled in the early part of the precipitation than toward the end.

3.3 Idiosyncrasies of Gelatin

The silver halide crystals are embedded in an organic matrix composed largely of gelatin, but also containing water, and in most emulsions, glycerol and other minor constituents. The analysis made by Ilford Ltd. finds for the gel a density of about 1.29 gm/ml at 58 % R.H.

The gel largely determines the mechanical properties of the emulsion, and it also plays an important part in the fundamental photochemical process. Its chief component, gelatin, has such remarkable characteristics that a review of the behavior of this truly wonderful material will be made.

Gelatin (M 54, EB 14) when hydrolyzed, is analyzable into a number of amino acids; the proportions of carbon, hydrogen, nitrogen, and oxygen in per cent being about 50.8, 6.9, 17.5, and 24.0, respectively. A small amount of sulfur may also be present and gelatin retains about 18-20 % water at 50 % R.H. The average molecular weight is in the interval 20,000 to 80,000 for various types, but fractions can be isolated with molecular weights that are lower and much higher. When gelatin, rather than glue, is to be prepared the extraction is halted earlier and carried out at a lower temperature, so that some of the strongly adhesive components are not present in the gelatin. Gelatin has great mechanical strength, however, so that when dried on glass, it is capable of being attached so strongly that the surface layer of glass may be broken loose and lift with the gelatin, as shown in Fig. 3.3.1. Gelatin dried without plasticizer on a glass plate may bend and break it.

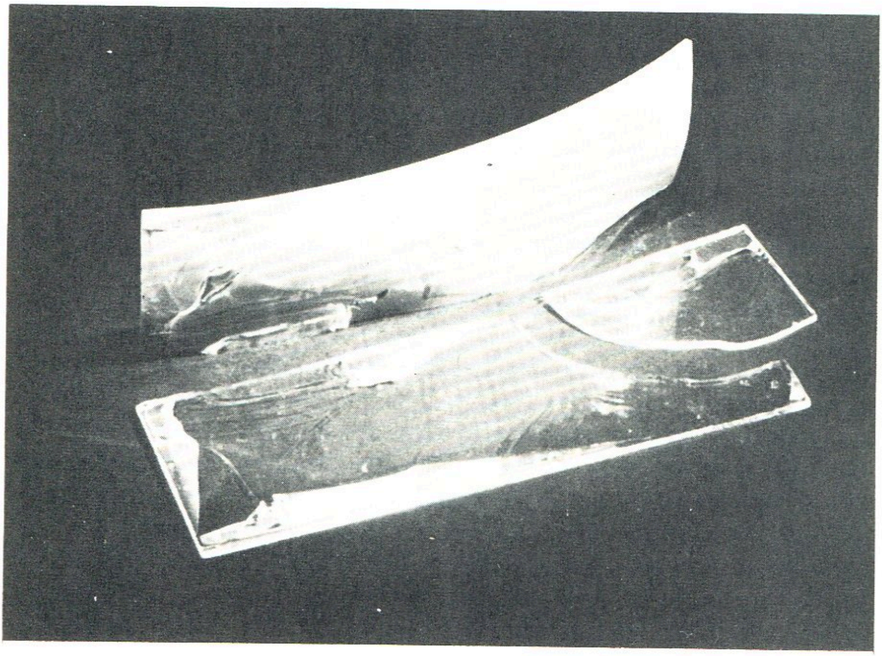

FIG. 3.3.1. A 1 × 3 inch plate after prolonged drying of the 1000 μ emulsion layer. Note that the glass surface has been pulled away. (Photograph by A. Oliver.)

Photographic gelatin is usually made from clippings of calf hides, ears, and certain other pieces. Some, however, is made from pigskin or bone. Collagen which is hydrolyzed to gelatin is the name of the material derived from hides, and the similar bone material is known as ossein. Two different extraction processes, lime extraction and acid extraction, yield gelatins of different photographic quality.

Gelatin is amphoteric. It acts as a good buffer in the vicinity of pH 10, and also in the region pH 2 to 5. At the isoelectric point (pH about 4.7) the volume, osmotic pressure, electrical conductivity, and the surface tension are at a minimum; the velocity, turbidity, and precipitability by alcohol are at a maximum. The force of cataphoresis is zero. Gelatin is insoluble in absolute alcohol, ether, chloroform, or benzene. It is completely precipitated from solution by an equal volume of saturated ammonium sulfate. Formaldehyde produces an insoluble precipitate with gelatin.

Gelatin swells greatly when soaked in water. As the swelling progresses, the gelatin becomes soft and is easily torn. At 35°-40° C it gradually melts to a liquid which may be diluted indefinitely. In concentrations exceeding 1 % it sets to a jelly when cooled. The viscosity curve of gelatin changes as the isoelectric point is reached; either a minimum or a break occurs depending on the age of the gelatin. Swelling is at a minimum at the isoelectric point. It reaches a high maximum at pH 2.7, then decreases in solutions of greater acidity; finally the gelatin goes into solution. Lime process gelatin does not swell as much as acid gelatin between pH 5 and 8. Above pH 11 both become greatly swollen, and at about 11.6 solution occurs. The swelling is affected by temperature because of the temperature-dependence of the ionization of the lysine component of gelatin. Swelling is generally less in a solution of an inorganic salt; and the swelling is greater in cold water. The behavior of gelatin changes as it ages and its behavior depends on temperature in a complex way.

The equilibrium of gelatin with water vapor shows a hysteresis effect. Also, the total volume contracts slightly and heat is evolved. The moisture taken up for a fixed relative humidity depends on the pH to which the gelatin was adjusted before drying. It rises rapidly as the pH is raised, and levels off after passing the isoelectric point, but no discontinuity occurs.

The value of gelatin as a photographic emulsion matrix derives from a combination of its properties. It is stable; components of the gelatin provide photographic sensitization; it permits penetration of solutions; and keeps grains dispersed so that clumping is avoided. It is strongly adsorbed to the silver halide crystals. It does not prevent the growth of a grain during emulsion manufacture, provided that ammonia or soluble halide is present to act as a solvent for the silver halide.

It is thought by some writers (M 54) that the sensitivity of an emulsion depends on the silver ion combining power of the gelatin. This is the silver that combines with the gelatin in such a way that it cannot be titrated with KBr or KI. Sulfur is a trace material in gelatin that affects its photographic behavior. Sheppard (SH 30) showed that allyl mustard oil or a similar material is present in gelatin to give it its sensitizing property. He showed also that an active form of sulfur produces silver sulfide on the surface of the crystals. An excess of such labile sulfur may tend to produce fog, and some forms are more useful than others for sensitization.

The behavior of gelatin is profoundly affected by hardening or tanning, usually brought about by chemical means; especially $K_2Al_2(SO_4)_4 \cdot 24H_2O$. Chromium is also important for tanning. Alum hardening causes a large increase in the gelatin melting temperature, but the effect has a different pH-dependence when the gelatin is bathed in the alum solution than when the alum is added to the gelatin solution. Gelatin is also hardened by halogens (suggesting a theory of solarization), by aldehydes, ketones, quinones, and by oxidation products of organic developers. Such an organic agent as formaldehyde acts as a hardening agent at high pH for lime gelatins. Hardening reduces the emulsion swelling and it increases the temperature required for solution in water.

An effect known as reticulation affects gelatin on photographic plates when the plate has been immersed in warm water ($> 20°$ C), or in water much warmer than the processing solutions. The surface becomes crackled; silver grains migrate and tend to collect on the ridges.

As a matrix material, gelatin has a number of obvious disadvantages. One is its swelling with increased humidity. Gelatin does not remain strong and rigid when wet. It often distorts on drying. The properties of gelatin vary rapidly with pH, and it is subject to damage by microorganisms. Gelatin is an animal product, and therefore is not completely under control with respect to its composition. Emulsion manufacturers must resort to blending of gelatins. For these and other reasons, some thought has been given to finding a material to replace natural gelatin. Polyvinyl alcohol, nylon, polypeptides, polyvinyl acetate, and others have been considered possible replacements. Because gelatin is cheap and has an amazing number of useful properties that are difficult to synthesize, no real competitor has yet been found.

According to Anosova *et al.* (A-U 60) a large fraction of the gelatin in NIKFI emulsion can be replaced by surface-active materials, and polyvinyl alcohol. These have the effect of increasing the colloidal stability of the emulsion and improving its physical properties. It has been observed, too, that the swelling versus pH curve of Ilford emulsion is quite unlike that of gelatin.

Therefore one cannot assume blindly that the behavior of emulsion gel is the same as that of gelatin. There are many reasons to believe that manufacturers of nuclear research emulsions may alter the gel so that it no longer has the properties of natural gelatin. A patented process