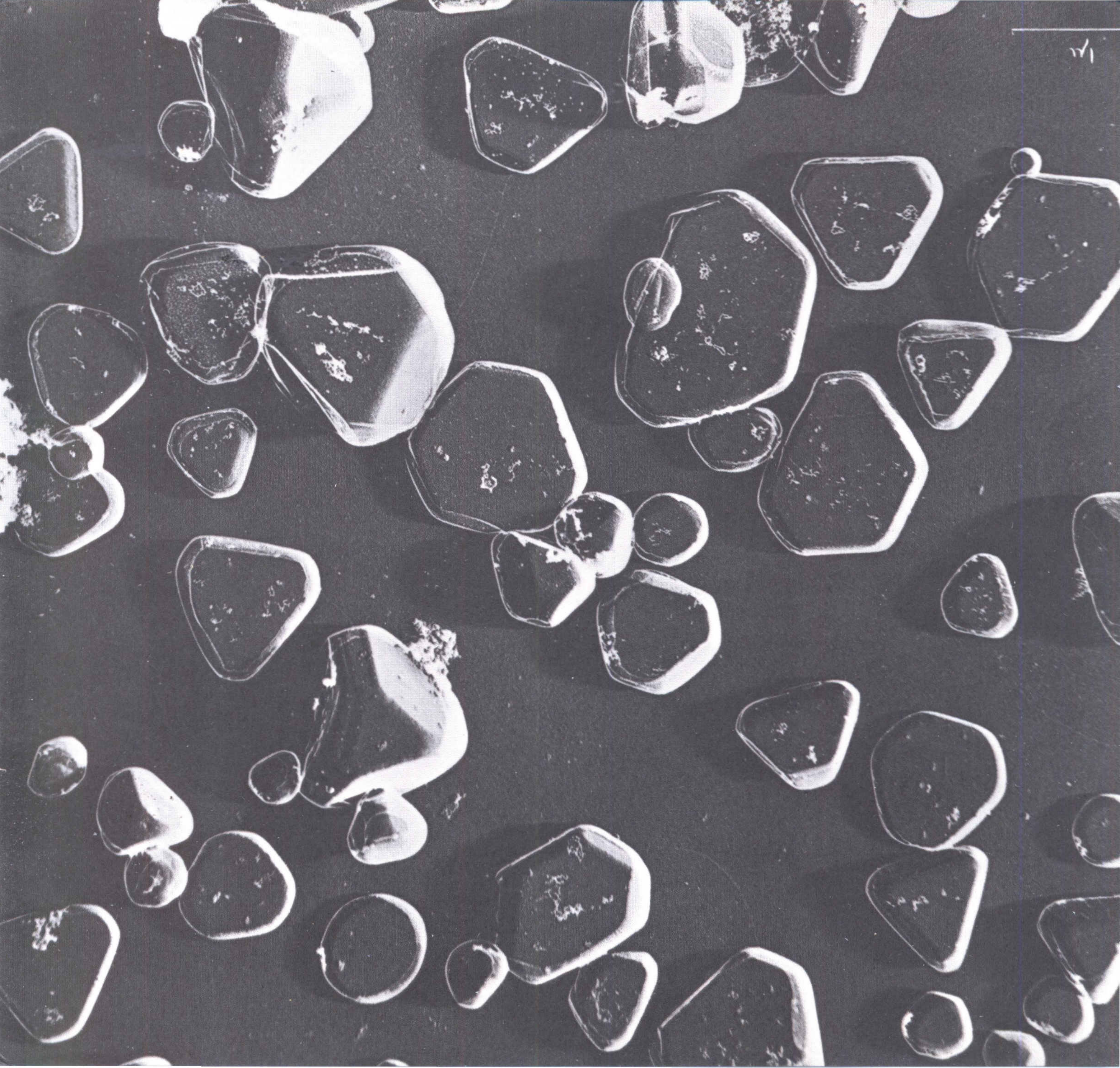
Chemistry Background Book

Pictures in Silver



Life as we know it today would be very different without photography. In the 150 years or so since the first crude photographs were produced, the techniques have been continually improved and the applications extended. Today photography touches most of our experience – the arts, the sciences, commerce, even the waging of wars, at some point or another.

Before photography became such a versatile tool, people used to argue about whether photography was an art, a craft, or a science. The derivation of the word, from the Greek *phos*, light, and *graphos*, writing, did not help. Like many similar arguments, where the opponents try to fit words into compartments, it was all rather pointless. Photography can be any of these things, and is often all of them at the same time.

If we look at the wonderful still photographs of Henri Cartier-Bresson, the haunting collection that was put together in 1963 for the New York Museum of Modern Art by

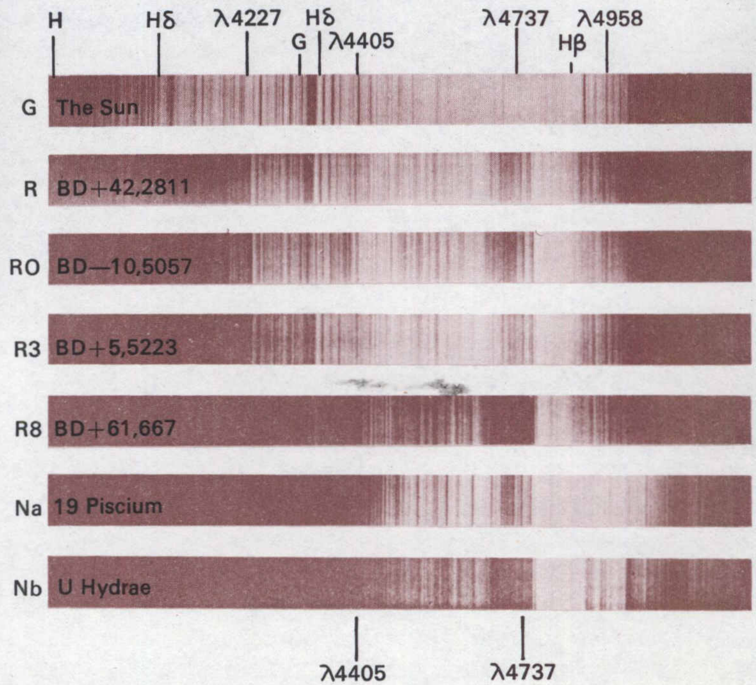
This still photograph is from *The Seventh Seal*, the best known film of a distinguished Swedish director, Ingmar Bergman. Consider the use of light and shade in this scene, the atmosphere created by ragged clouds and a sullen sea. On the strength of what you see, do you think that photography is an art form? *British Film Institute*

Edward Steichen under the title 'The Family of Man', or the motion pictures of the great Swedish director Ingmar Bergman, we are bound to admit that photography is an art, at least in terms of how it reveals the excitement and pathos of the human condition.

On the practical side, in the sense of being more immediately and obviously useful, the applications of photography are endless. Physicists use photography to take pictures of everything in the natural world from lightning flashes to the tracks of atoms, and with it astronomers appear to stop the planets in their motion. Doctors use photography to study diseases and surgical operations, and engineers take pictures of things that move too rapidly to be seen by the unaided eye – rapidly moving parts of engines, for example. Archaeologists discover buried cities by photographing the ground from aeroplanes. The police use photography to catch criminals. Advertising men use it to sell their products to the public. Military experts photograph the territory of potential

Woodhenge was a mainly timber structure in Wiltshire standing only two miles from Stonehenge. Time appeared to have removed all traces of its existence as a centre of pagan worship, except the stones seen in the lower ring. The postholes marking the other circles were first observed on an aerial photograph. A bird's-eye view of the terrain can reveal archaeological features not visible to observers at ground level.
Aerofilms & Aero Pictorial Ltd.

Photography enables astronomers to record the stars and helps them to make a three-dimensional pattern of the night sky. The Great Spiral in the constellation, Andromeda, has a well defined structure, the plane of which is tilted when seen from the Earth, giving it an apparently elongated form.
Royal Astronomical Society



The chemical compositions of stars may be determined from photographs of their spectra. A camera can record simultaneously the spectra of many stars by placing a prism over the camera objective.
Royal Astronomical Society

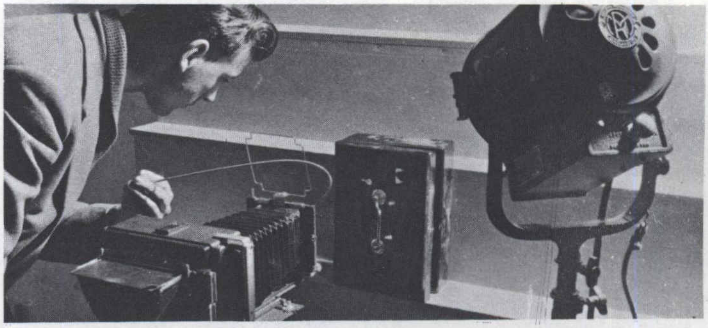
enemies. Weather men predict the paths of hurricanes by photographing them from satellites hundreds of miles above the Earth. And you and I bring along our cameras on holiday in our millions, to take snaps and colour slides.

To supply these varied needs, photography has grown into a huge industry, especially in the United States, Germany, and Japan, where the world's biggest photographic manufacturers have their headquarters. Vast numbers of cameras and astronomical quantities of films and printing papers are manufactured every year. In the United Kingdom, for example, of the total consumption of silver – which, as we shall see in a moment, is a very important substance in photography – over 40 per cent goes into the manufacture of photographic film.

Apart from silver, photography requires a great many chemical substances – developers, fixers, hardeners, reducers, intensifiers, dyes, and so forth. Their manufacture is a substantial sector of the chemical industry, employing millions of people in research, manufacture, and selling.

A global photomosaic made from 450 individual pictures taken by Tiros IX weather satellite during the twenty-fours hours of 13 February 1965. This first complete view of the world's weather shows how space flight technology plus photography may be used to provide reasonably accurate forecasts of weather conditions.
U.S.I.S. American Embassy

Photography plays an important part in routine police procedure and in crime detection. It can be used to record traffic accidents, detect forgery, identify criminals, and, as this picture shows, to provide a record of finger prints. A set of finger prints on the rifled deed box may be the vital link in the chain of events leading to 'an early arrest'.

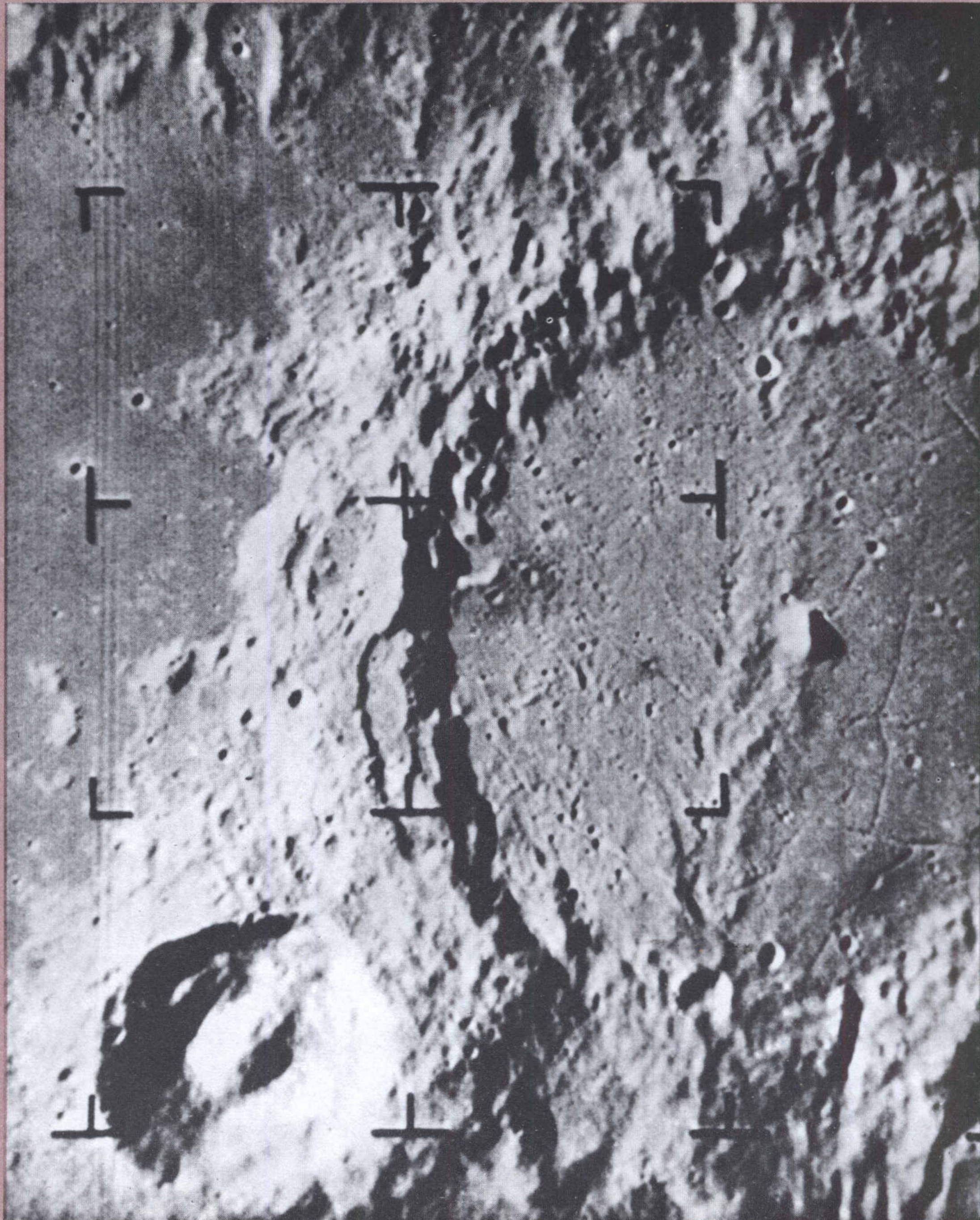


yesterday

For thousands of years man has been fascinated by the strangely scarred surface of the moon. Telescopes proved that there was no 'man in the moon', only a bleak, cratered no-man's land devoid of life. The photograph above was taken over a century ago.
Crown Copyright. Science Museum, London

today

(*Right*) A picture of the moon's surface taken by a camera in Ranger 9, 258 miles or 2 minutes 50 seconds before impact.
U.S.I.S. American Embassy



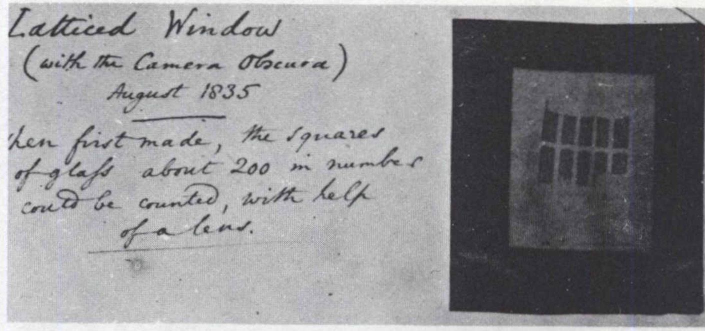
Early days – The question of who 'invented' photography cannot be settled. It is a commonplace in the history of science that the same discovery is often made independently but more or less simultaneously by different workers. In any case, the exact moment at which an idea is born is usually obscured because people build upon and adapt the inspirations of their predecessors.

'Photochemical' effects like the fading of dyes had been known for hundreds of years. But it was not until 1727 that a German scientist in Altdorf called Johann Schulze showed that sunlight would darken certain silver salts. In fact, the darkening (though its connection with light was not understood) had been observed long before. Schulze exposed papers coated with silver salts to strong light. Sometimes he covered the papers with stencils: the exposed areas showed as distinct and darkened patterns which could in a sense be described as negatives.

The great Swedish chemist, Wilhelm Scheele, and others extended Schulze's work and in 1777 Scheele discovered that the rate at which the silver salts darkened depended upon the colour of the light: violet caused rapid darkening while there was no reaction at all with orange or red. These scientists of the eighteenth century laid the foundations of photography but they were unable to fix the images – to make them permanent. The lighter areas of their silver salt preparations would darken slowly so that the outlines of the dark image disappeared.

The first fixer to be discovered was sodium thiosulphate ($Na_2S_2O_3$). It is commonly called 'hypo' from its earlier (and inaccurate) name sodium hyposulphite. Hypo was first made in 1819 by Sir John Herschel, the celebrated English astronomer, who showed that it would dissolve silver chloride.

This photograph of a latticed window is one of the earliest known and was taken by William Fox Talbot at his home, Lacock Abbey, in 1835 – two years before Queen Victoria's accession to the throne.
Science Museum, London



An English clergyman with an interest in chemistry called J. B. Reade and the more celebrated photographic pioneer Fox Talbot applied this discovery to photography in the late 1830s. They used silver chloride as the light-sensitive chemical, and hypo to dissolve the silver chloride unaffected by light during the exposure of the preparation and formation of a photographic image. The result was that the unaffected parts could not darken later, so that the image was fixed.

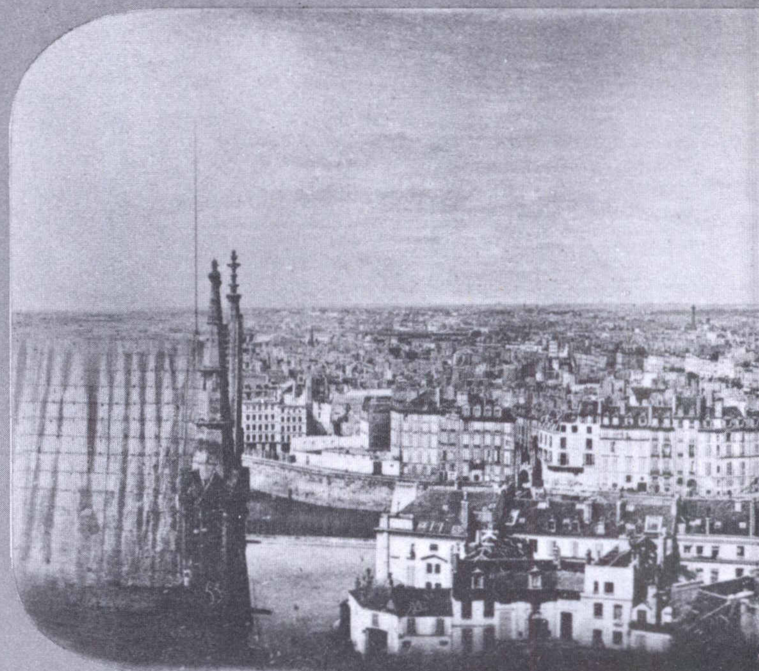
Nothing was known about 'developing' an image. The chemicals were simply exposed to bright light for a long time in order to produce a pattern. A fundamental feature of modern photography is that silver salts are exposed to light for a very much shorter time than is required to produce a visible darkening. The first step is a brief exposure of a chemical to a pattern of light. The image is developed later by chemical means.

Silver salts were not the only light-sensitive substances used by the early experimenters. The Frenchman Niépce, for example, found that bitumen, when exposed to light, became insoluble in oil of lavender, and this made it possible to produce a type of relief photograph after about eight hours.

'The Chess Players' (*circa* 1845) – an early Calotype by Fox Talbot.
Crown Copyright. Science Museum, London

Daguerreotypes were silver plates coated with silver iodide. After exposure to light in a camera these plates were treated with mercury vapour which attacked the exposed parts of the iodide layer and produced a positive image.

This panorama of Paris in 1844 is a fine example of a Daguerreotype, remarkable as much for its clarity as for the fact that it shows a Paris almost unknown to modern eyes.
Crown Copyright. Science Museum, London



This work with these rather strange materials is of interest because certain modern methods of photoreproduction depend on similar processes.

It was also in the late 1830s that Louis Daguerre in Paris discovered a process that embodied a kind of development of the photographic image. His famous Daguerrotypes were plates of silver coated with silver iodide by holding them in iodine vapour. The plates were exposed to light in a camera and then treated with mercury vapour; the mercury attacked the exposed parts of the iodide layer and produced a positive

image – light where the light had fallen and dark elsewhere.

The next step forward came when Fox Talbot patented his Calotype process in 1841. He used transparent paper impregnated with silver iodide and washed in gallic acid and silver nitrate immediately before use. The paper was then developed in gallic acid and fixed, washed, and dried. The modern idea of development, in which the small changes caused by a relatively short exposure to light are subsequently multiplied millions of times (and rendered visible to the eye) by a chemical developing agent, had become established at last. It is the multiplicative effect of developing that gives modern photography its versatility, because it makes it possible to produce an image from a film or plate after it has been exposed to light for only a fraction of a second – a much shorter interval of time than is needed to produce visible darkening.

The chemistry of photography – The chemical reactions involved in photography, particularly colour photography where there is a great variety of processes to choose from, are much more complicated than might seem at a first glance. An understanding of the subject is further hindered by the secrecy behind which the manufacturers, for obvious reasons, conduct their research, and by the rapid pace of progress.

It is difficult to see any limits to the technical developments that are possible. Today's films are many times more sensitive than those of a few years ago, developers are better, and processing is quicker, easier, and more reliable. It may be that one day we shall all be making our photographs in a completely different way, without the assistance of the silver salts on which our present black-and-white and colour processes depend, but that day is not yet in sight.

As for present-day photography, the core of the whole thing is that when a ray of light strikes a crystal of these sensitive silver salts (chlorides, bromides, or iodides) some very strange things happen. A small dark deposit of metallic silver is formed and can be made to appear by using a developer, and these tiny groups of silver atoms eventually form the dark parts of a photograph. In its simplest form, the reaction may be expressed as follows:

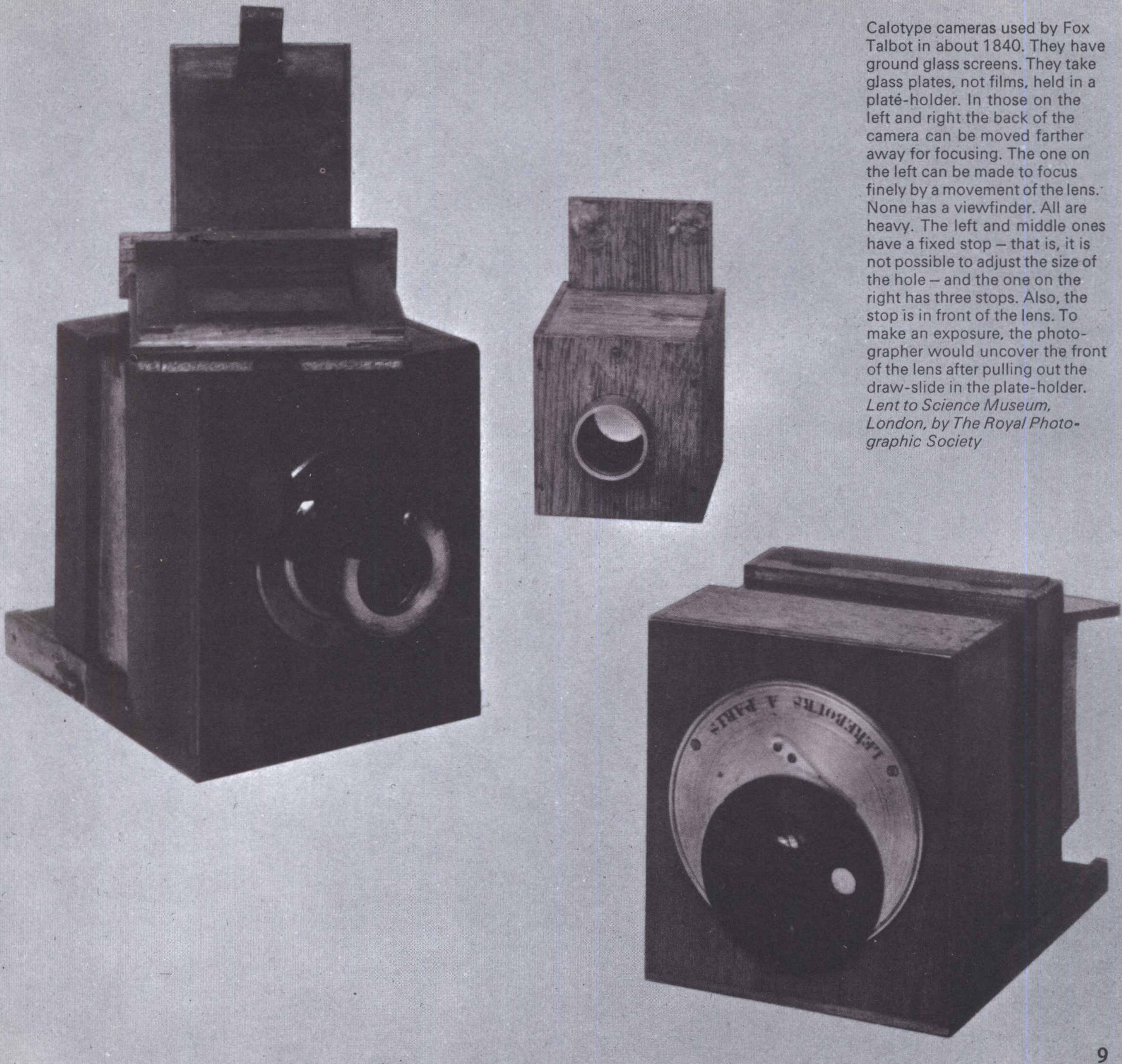
$$Ag^{+}Br^{-}(c) + \text{light energy} \rightarrow Ag + Br$$

A great deal has been written about the precise mechanism by which the reaction comes about but, before it can be understood, we must know something about the materials used in photography and the way in which they are used.

Making a photograph – Most cameras have a lens to focus an optical image on the film or plate, a variable diaphragm to control the brightness of the image, and a mechanical shutter that is adjusted to determine the exposure – the length of time the image rests on the film. There are many variants of these basic features.

The old box camera usually had a fixed shutter speed; many modern cameras have 'electric eyes' – photocells that generate enough power to adjust the diaphragm according to the brightness of the subject. Pinhole cameras have no lens, the image being formed by rays of light passing through the tiny aperture. You can see this effect quite easily by making a hole in a piece of paper with the point of a pencil, holding the paper up to the window, and moving another piece of paper behind it to catch the image of the window. A good lens, however, gives a sharper and much brighter picture.

Whatever the camera, most photography requires that the optical image of the subject should be allowed to fall on a layer of light-sensitive emulsion carried on a transparent film or plate for as little as a thousandth of a second to about a fiftieth; in special circumstances, even shorter or very much longer exposure may be necessary. The effect of this is to create in the emulsion a corresponding latent image which is then developed. This is always a negative image – dark where the light has fallen on the emulsion and light where it has not. In the case of so-called reversal films, the image is inverted black-for-white by bleaching away the dark silver image and giving the film a further exposure to light. The parts of the emulsion that are at first unaffected become dark on a second treatment with a developer, giving a positive image. Transparent positives for viewing with a projector or any other device that uses transmitted light are frequently



Calotype cameras used by Fox Talbot in about 1840. They have ground glass screens. They take glass plates, not films, held in a plate-holder. In those on the left and right the back of the camera can be moved farther away for focusing. The one on the left can be made to focus finely by a movement of the lens. None has a viewfinder. All are heavy. The left and middle ones have a fixed stop – that is, it is not possible to adjust the size of the hole – and the one on the right has three stops. Also, the stop is in front of the lens. To make an exposure, the photographer would uncover the front of the lens after pulling out the draw-slide in the plate-holder. *Lent to Science Museum, London, by The Royal Photographic Society* made by a reversal process. Most amateur cinematograph films are made in this way (only one copy, of course, is obtained) and most manufacturers market at least one reversible colour film.

When a film has been developed, it is usually washed to remove the greater part of the developer adhering to it or absorbed in the emulsion. It is then fixed to remove the unchanged silver salts, hardened by means of chemicals (often already present in the fixer) that strengthen the soft, easily damaged emulsion, washed again very thoroughly to remove the fixing and hardening chemicals, and finally dried. If the final product of this process is a negative, it can be put in an enlarger and its image (or a part of it, as the photographer wishes) projected on to a piece of emulsion-coated paper or another photographic plate to give any number of positive prints or transparencies, each of which is processed by a series of steps similar to those used to make the negative.

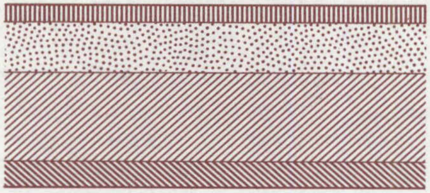
By contrast with the cameras on page 9 here are two modern cameras.

The one on this page is for the ordinary amateur but it is still comparatively sophisticated. There is nothing in front of the lens. The stop is inside, between the glass and the lens, and is altered by the slide lever for 'sunny' or 'dull', according to the light.
The exposure is made simply by pressing down the lever. The film (not plate) is uncovered all the time and is changed by winding a fresh piece into the gate by means of the large ridged knob. There is a viewfinder so the photographer can see what picture he is taking all the time. The camera is smaller and lighter than the early ones.
Courtesy of Kodak Ltd.

Plates, films, and papers – The sensitive materials with which photographs are made all consist of a light-sensitive emulsion coated on a support. Glass plates were used long before the flexible supports now used in roll-film, and the rigidity and high transparency of glass are still necessary for some kinds of photography. Nevertheless film, with its flexibility and light weight, has superseded glass plates for most purposes. George Eastman, the founder of the Kodak empire, was the first to put roll-film on the market, and he used cellulose nitrate for the transparent support. Nitrate film is highly inflammable,

(*Right*) A highly elaborate model for the professional or gifted amateur. It is a single lens reflex camera which uses 35 mm film. It has a focal plane shutter with speeds from one second to 1/2000 second, synchronized for flash bulbs and electronic flash. The scene is viewed through the taking lens and therefore the eye sees exactly what will reach the film. This is the characteristic of reflex cameras and is achieved by a mirror inside the camera which automatically moves up and out of the way at the moment of taking the picture. The mirror returns again after the picture is taken and so the camera is now ready for the next picture. The lens, a 50 mm f/2 Summicron–R, has an angle of view of 45°, which is standard on 35 mm cameras. There is a built-in exposure meter which measures the light being reflected from the subject and indicates what is the correct exposure. Also, the lens has a fully automatic diaphragm. That is, at rest the diaphragm is fully open to permit maximum light for viewing, and during an exposure it closes automatically to the pre-selected aperture.
Leitz-Leicaflex

Section through a typical film



however, and was soon ousted by cellulose acetate. Modern films have a tri-acetate support, which is stronger than the mono-acetate and less affected by humidity.

Strictly speaking, the 'emulsion' is not an emulsion at all, but a suspension of tiny silver halide crystals in gelatin. Many of the manufacturing details of today's highly sophisticated emulsions are closely guarded secrets.

There are many types for special purposes, but most of them are made by mixing silver nitrate with an excess of potassium bromide (in the presence of gelatin) to precipitate crystalline silver bromide. The crystal size is controlled by 'ripening' – holding the precipitated material at a constant temperature for some time. This allows the smallest crystals to redissolve and the larger ones to grow, and has a profound effect on the sensitivity of the film: large crystals produce faster and more sensitive emulsions. After ripening, a batch of emulsion is cooled to make it set, and is then shredded and washed. Finally it is mixed with more gelatin of a special type and digested – maintained at about 60°C for several hours – before being coated on the support. This special gelatin contains certain sensitizing sulphur compounds which, during digestion, become adsorbed as specks of silver sulphide on the silver bromide crystals, and make the emulsion even more sensitive. The gelatin is made principally from cowhide, and it has been found that the sensitizing compounds, which are related to allyl mustard oil, originate in the seeds of black mustard and other plants of which cows – fortunately for photography – are very fond.

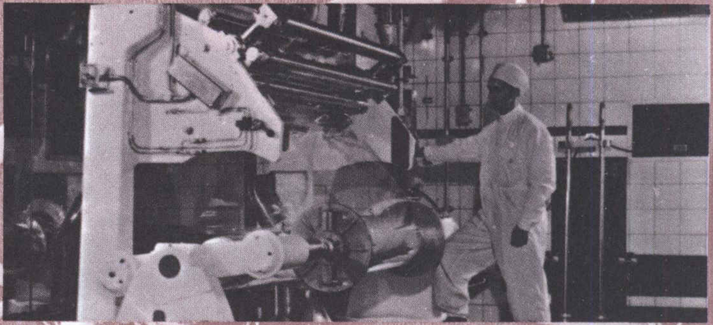
Silver chloride and silver iodide (but not the fluoride) are also used in some emulsions. The chloride, which is insensitive to visible light, is used mainly in printing papers for making positives, where it responds readily to the ultraviolet radiation present in the printing light. Most modern emulsions contain a few per cent of silver iodide to increase their sensitivity in the blue-green part of the spectrum. Panchromatic emulsions, which are designed as the name implies to be sensitive to light of all colours, embody added dyestuffs which increase sensitivity to red and yellow light.

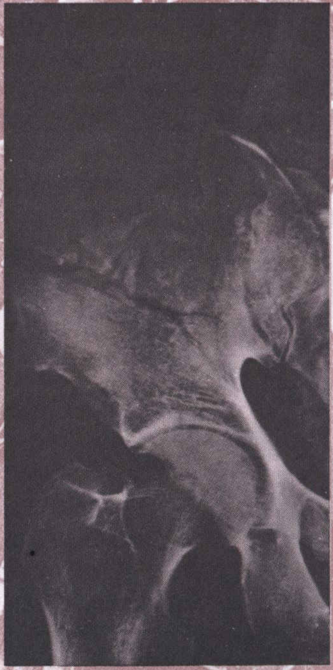
An emulsion is usually given a thin outer skin of gelatin to protect it from abrasion, and the back of the film support is often coated with a dyestuff to absorb any light that may pass right through the film during exposure. This cuts down reflections from the back surface of the support, and minimizes 'halation' – the ring of diffused light that can often be seen surrounding an intensely bright highlight on the photograph.

Printing papers for positives are similar, although the emulsions can be produced more quickly because graininess (large crystal size) is less important. High-grade printing papers have a baryta (barium sulphate) coating under the emulsion to provide an optically smoother surface to reflect light efficiently. Contact papers deserve special mention because the emulsion is made with silver chloride instead of the bromide. This makes it possible to handle papers safely in a certain amount of artificial light, and explains the old name 'gaslight paper'.

Undeveloped polyhedral silver bromide crystals, photographed under an electron microscope (×21,000).
Ilford Ltd.

Film base (*below*) comes in the form of rolls, 40-50 inches wide and 2,000 feet long. It is known as safety base, and is made of cellulose esters (complex materials derived from cotton). The base will be coated with layers of emulsion, a suspension of finely divided silver salts in specially treated gelatin.
Courtesy of Kodak Ltd.

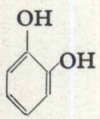


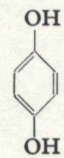


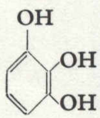
(*Left*) X-rays were discovered in 1895 by Wilhelm Röntgen. The fact that many substances are transparent to X-rays which in turn affect photographic emulsions resulted in the development of radiography. This example of its use in clinical diagnosis reveals a fractured hip-bone.
Courtesy of Kodak Ltd.

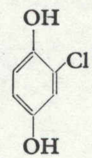
Developing agents – Photographic developers are reducing agents – that is, they act as suppliers of electrons and are themselves oxidized in the process. The emergence of an image depends upon the fact that silver ions in those crystals which have been exposed to light are reduced at a much faster rate than others. But developers will also attack unexposed crystals if, for example, development is allowed to go on too long or at too high a temperature. Indeed, some unexposed crystals are always affected during development, which leads to a slight overall greying of the emulsion called fogging. A good developer is so formulated that it can reveal the latent image to the required degree of contrast before the general fogging of the emulsion becomes significant. To counter fogging, potassium bromide is added. This substance has much the same effect on an over-vigorous developer as it has on human beings – it slows it down.

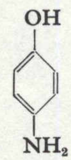
The search for new and better developers goes on all the time, and many hundreds have been launched on the market in the last fifty years. Most of them have since quietly disappeared again. As things are, fewer than a dozen are of any real importance – though no one can say, of course, what is going to happen tomorrow. Some of the best known are shown below:

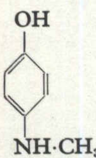

catechol

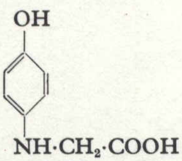

hydroquinone

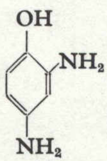

1,2,3-trihydroxy-benzene

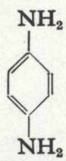

chloroquinol


p-aminophenol


p-methyl-aminophenol (metol)


p-hydroxyphenyl-glycine

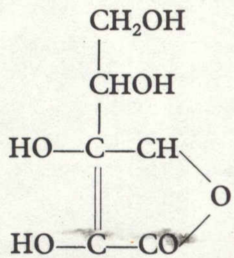

amidol


p-phenylene-diamine

There have naturally been attempts to identify in the molecules of these compounds a grouping that might be characteristic of good developing agents. This is a standard practice of the research chemist in any industry: if he has reason to believe that a certain grouping of atoms will confer the property he is interested in, he can go on to synthesize new compounds containing the grouping and expect that these, too, will have the same property. The best that has so far been achieved with developing agents appears to be the Kendall-Pelz formula:

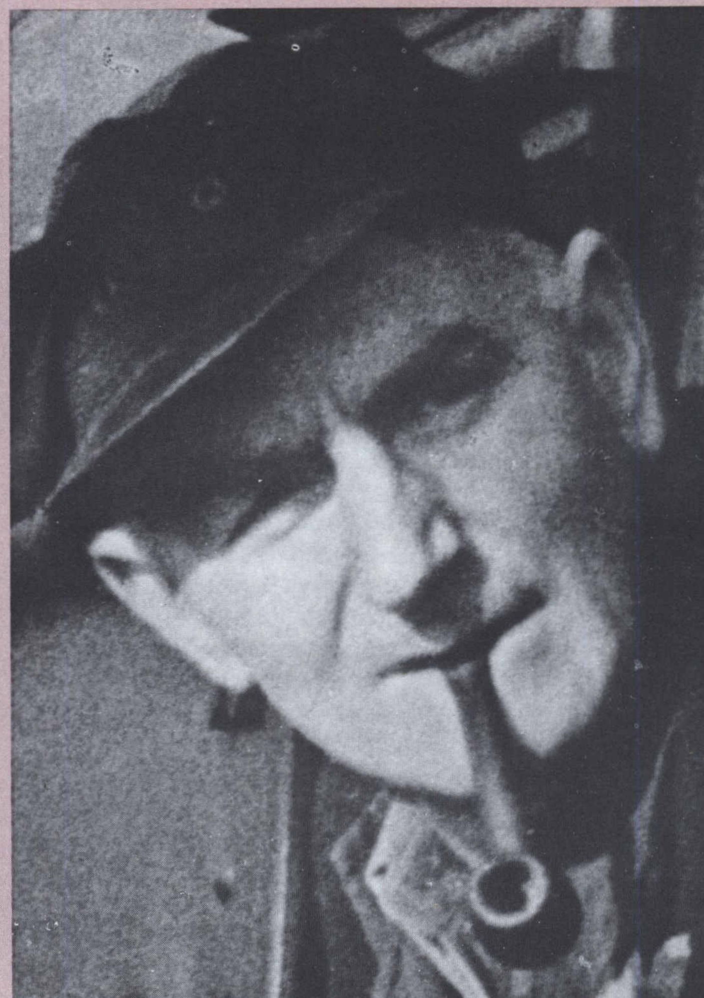
R_1—(—$\overset{|}{C}$=$\overset{|}{C}$—)$_n$—R_2, where R_1 and R_2 are hydroxy (—OH) or amino (—NH_2) groups.

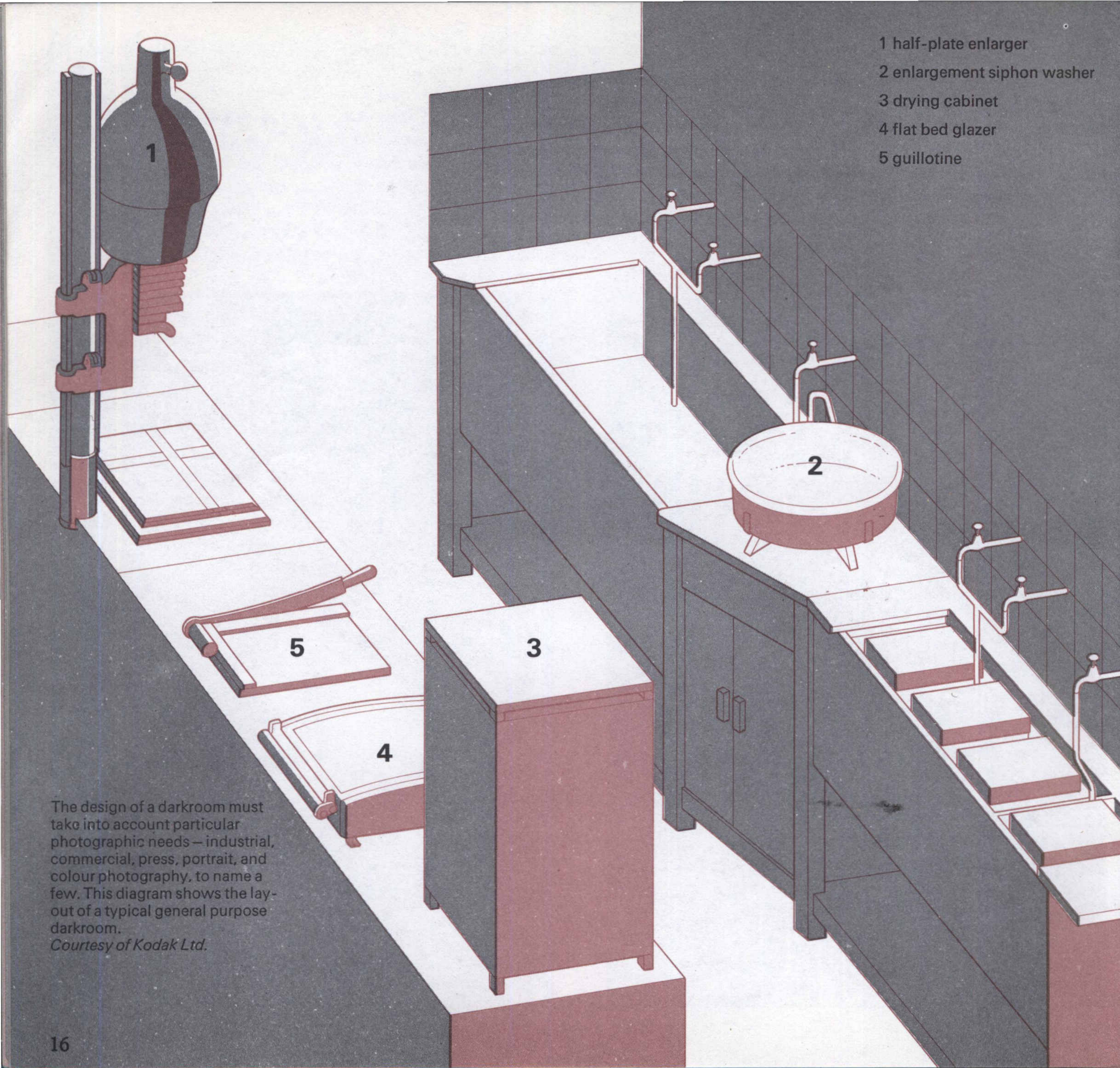
It is interesting to note that when *n* is zero the formula gives the inorganic compounds HOOH (hydrogen peroxide), NH_2OH (hydroxylamine) and NH_2NH_2 (hydrazine), all of which have some activity as developing agents, though not commercially. Another substance that fits the formula (n=1), and which could be used at a pinch as a developing agent, is ascorbic acid (Vitamin C).



Many popular developers contain two of the well-known developing agents, and in some cases the mixture exhibits superadditivity, each agent appearing to enhance the activity of the other.

A developing solution causes particles of the silver salt in the gelatin to cluster together – the effect is of grains. The extent to which the grains are visible depends on the degree of enlargement (compare the two photographs). Grain size may also be influenced by prolonged development and over-exposure.
Courtesy of Kodak Ltd.





The design of a darkroom must take into account particular photographic needs – industrial, commercial, press, portrait, and colour photography, to name a few. This diagram shows the lay-out of a typical general purpose darkroom.
Courtesy of Kodak Ltd.

The developer at work – There are several theories about the mechanism which turns a latent image into a visible image by the use of a developer, but it will be sufficient for our purposes to outline the points on which the theories agree. All developers contain a solvent that will dissolve silver bromide. Usually this solvent is sodium sulphite, and silver and bromide ions pass into solution under its influence. The positively-charged silver ions tend to migrate to the silver nuclei already established in the latent image, and are reduced to atoms of silver by the electrons supplied by the developing agent.

The grains of metallic silver grow during development in a way typical of many crystals, the silver atoms building up in long tangled filaments, growing outwards from the specks of the latent image. The bromide ions combine with hydrogen ions to form hydrobromic acid, which gradually decreases the alkalinity of the developer and may eventually render it more or less inactive.

In addition to its role as a solvent, the sodium sulphite helps to maintain the alkalinity of the solution in the developing bath by neutralizing the hydrobromic acid. However, other alkaline substances – notably borax, carbonates, amines, and even caustic alkali – are usually added as well because, generally speaking, the higher the alkalinity, the more vigorously the developer acts, working faster and producing an image of higher contrast.

Fixers – Once the visible image has been fully developed on the plate, the crystals of silver halide in the emulsion have served their purpose (unless reversal is intended). But most of the crystals – something like three-quarters, on the average – remain unchanged, having been insufficiently exposed to become reducible. They are still sensitive to light, however, and must therefore be removed from the emulsion as completely as possible. This fixing process is carried out by chemicals that convert the unchanged silver halides to water-soluble compounds that can be removed by washing.

Apart from their ability to combine with silver halides, good fixing agents must be cheap and harmless to the silver image, the gelatin, and the photographer. Most of the compounds that meet these requirements contain sulphur or nitrogen, though common salt can be used if nothing better is available. Incomparably the best fixing agents so far discovered are the thiosulphates, and sodium thiosulphate is the cheapest and the most popular.

In spite of the fact that hypo has been in use as a photographic fixer for something like 130 years, it was not until 1953 that the chemistry of the fixing reaction was explained satisfactorily. It was shown then that the principal reaction (subsidiary ones probably take place to a small extent) is $AgBr(c) + 2S_2O_3^{2-}(aq) \rightarrow [Ag(S_2O_3)_2]^{3-}(aq) + Br^-(aq)$. This silver compound is then washed out of the emulsion with water.

Fixing solutions are usually acidified to stop the action of any developer that is carried over from the developing bath, and to prevent staining caused by oxidation products of the developing agent. The acidification of hypo solutions, however, tends to produce a precipitate of sulphur because it liberates thiosulphuric acid, which is unstable and breaks down to form sulphurous acid and sulphur:

$$H_2S_2O_3(aq) \rightleftharpoons H_2SO_3(aq) + S.$$

This undesirable eventuality (the sulphur can form a troublesome deposit on the emulsion) is controlled in two ways: the acidification of the fixer is carried out with a weak acid like acetic acid, which does less damage than mineral acids, and a quantity of sodium sulphite is incorporated in the fixer. The role of the versatile sulphite on this occasion is to provide an excess of sulphite ion in the solution to drive the reversible decomposition reaction in the opposite direction.

Both of these defences against sulphur precipitation can be achieved by a single additive, using potassium metabisulphite instead of acetic acid and sodium sulphite. The metabisulphite acts as a source of both weak acid and sulphite ions in the solution.

So that the acid in the fixer is not used up by large amounts of alkali from the developer, the film or print is usually dipped in a stop bath of dilute acetic acid between developing and fixing.

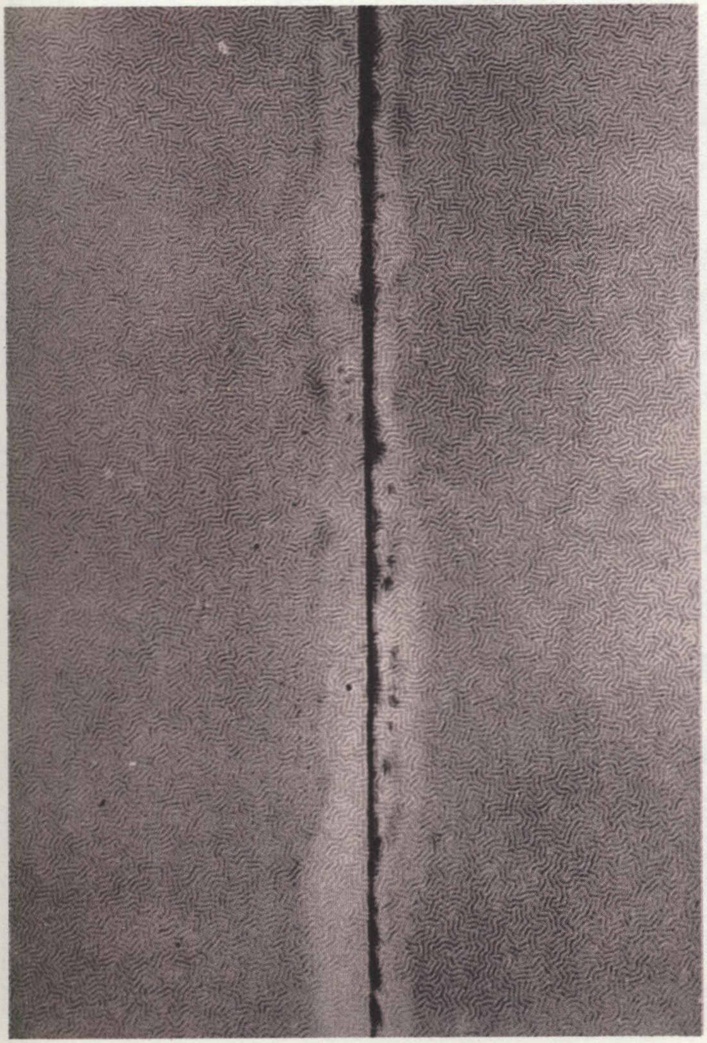
Hypo, in spite of its many useful qualities, also falls short of perfection in another way – it will dissolve silver grains, especially very small ones, and unnecessarily prolonged immersion in the fixing bath must therefore be avoided.

Most modern fixers also contain a hardening agent. Wet gelatin is mechanically weak, and is therefore very vulnerable to abrasion as well as heat distortion or even fracture ('reticulation' – see page 19) caused by temperature differences between the various processing baths. The hardeners most widely used today are alums – potassium alum or chrome alum – which are believed to work by forming strong cross-linkages between their metallic ions and the acidic carboxyl groups (and possibly also basic amino groups) of the gelatin. Formalin (an aqueous solution of formaldehyde) is also used as a hardening agent, though usually in a separate bath following the fixer.

Rapid fixers which contain ammonium thiosulphate rather than sodium thiosulphate are now available. These reduce the time necessary for fixing considerably.

Photographing substances under a microscope (microphotography) greatly contributes towards a detailed understanding of their structure. Here is a photomicrograph of niobium – treated steel (magnification × 1,200) showing the coarse-grained structure of this alloy.
British Iron and Steel Research Association

Wet gelatin is vulnerable to abrasion and distortion. A further hazard is fracture or reticulation. The net-like formation is caused by excessive temperature changes between the various processing baths.
Courtesy of Kodak Ltd.



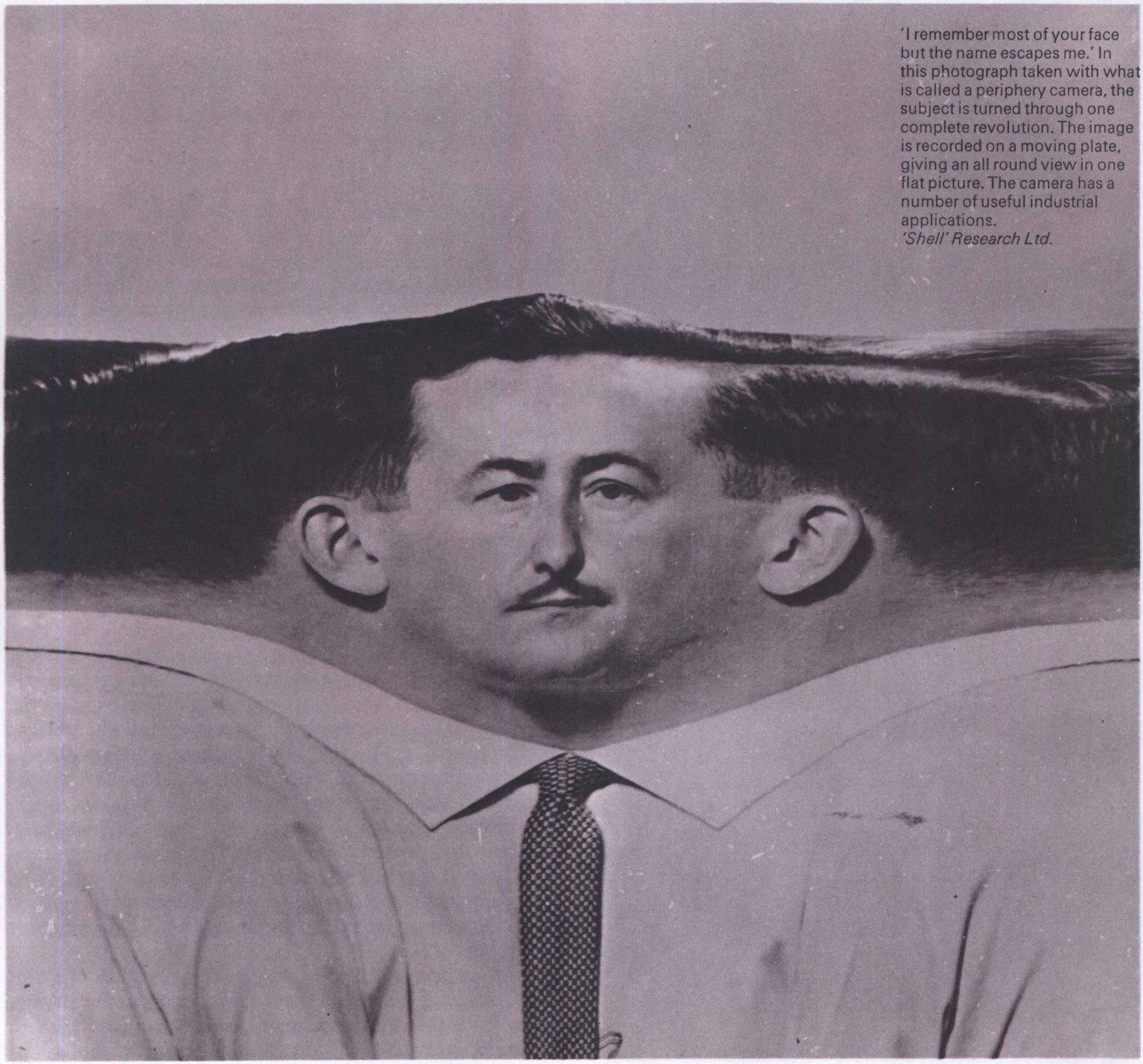
Washing and drying – After treatment with the fixer, the soluble silver compounds so formed must be washed away. A given quantity of wash-water will always dissolve the same percentage of the salts remaining in the emulsion, and it follows that a succession of washes with small quantities of water will remove more of the salts than the same total quantity of water employed as a single wash. Washing should therefore involve a large number of rinses (at least a dozen) in circumstances where the much more convenient alternative of washing the film for half-an-hour in running water cannot be used.

The dangers from sudden large changes in temperature to the physical structure of the emulsion are greater during washing. It should also be remembered that very hard waters, which tend to form annoying deposits of insoluble salts, may need softening either by boiling or with chemicals before use.

Solutions are available which make it possible to reduce the washing time from hours to minutes. These are useful, especially when photographic images of exceptional stability are required, as in the preparation of photographs for archives. The commonest of them is ammoniacal hydrogen peroxide, which oxidizes sodium thiosulphate to an extremely stable mixture of sodium sulphate and ammonium sulphate.

Fierce drying must always be avoided, however urgent the need for the finished photograph. Temperatures over 60°C may damage the emulsion, and total dehydration of the gelatin ruins the image; a 'perfectly dry' emulsion still contains about 10 per cent of water.

Wetting agents are often employed to prevent drops of water adhering to the film and leaving marks after drying. They lower the surface tension of the water so that it can no longer cling to the film in its usual stubborn fashion.



'I remember most of your face but the name escapes me.' In this photograph taken with what is called a periphery camera, the subject is turned through one complete revolution. The image is recorded on a moving plate, giving an all round view in one flat picture. The camera has a number of useful industrial applications.
'Shell' Research Ltd.

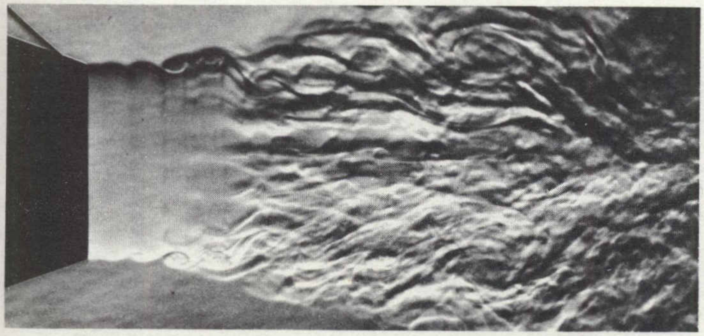
Altering the image – Students of photography are constantly (and very properly) exhorted to 'get it right on the negative' – in other words, to choose a film of suitable speed, grain size, and sensitivity across the spectrum, to expose it correctly, and to process it properly. This is undoubtedly the way to get consistently good photographs: the extent to which the image can be modified afterwards is small.

There are, however, two processes that can be used to effect marginal improvements in certain circumstances. One is called 'reduction' because it diminishes the intensity of the image. The other is called 'intensification' because it makes the image more dense.

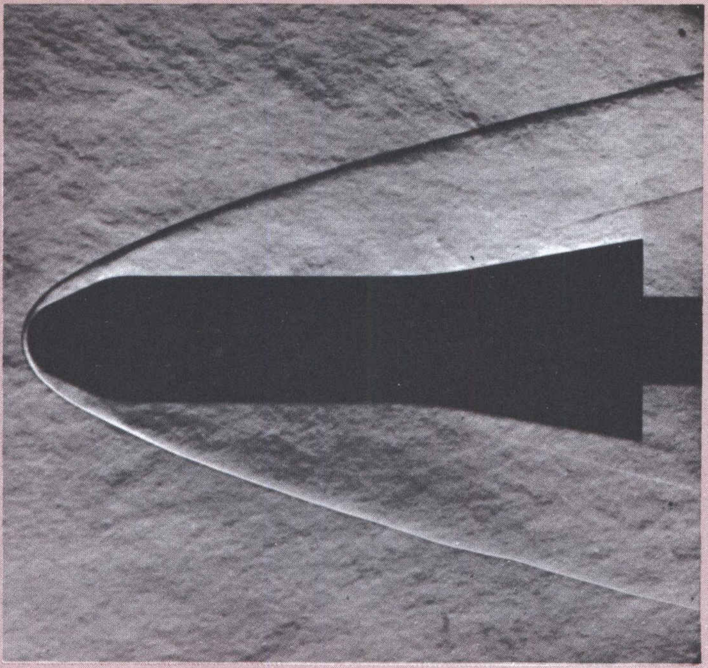
The name 'reduction' is an unfortunate one in so far as the process involves oxidation. However, the name is too firmly entrenched in the photographer's vocabulary to be dislodged now: about the only thing to be done is to call the chemicals used for this purpose reducers to distinguish them from true reducing agents.

Reducers fall into two chemical types: those that oxidize the silver of the image to water-soluble salts, and those that oxidize it to salts soluble in another chemical such as hypo. Many of the first type consist of sulphuric acid plus an oxidizing agent such as potassium permanganate, potassium dichromate, ammonium persulphate, or quinone; they convert some of the silver to water-soluble silver sulphate. The most popular reducer of all – Farmer's reducer – is an example of the second type. Farmer's reducer is a mixture of potassium ferricyanide and hypo; it oxidizes the silver to silver ferrocyanide which dissolves in the hypo. Other reducers of this type employ potassium bromide, which rebrominates the silver to silver bromide.

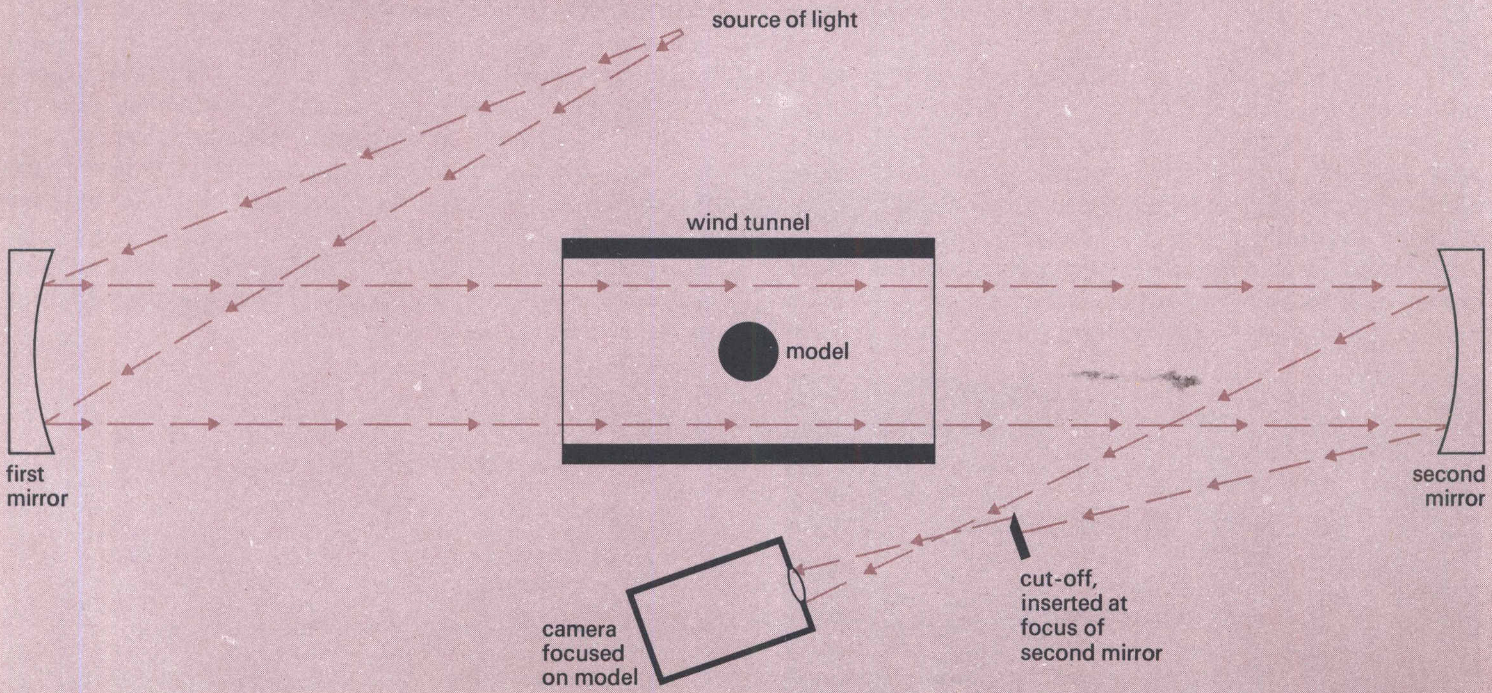
Intensifiers work either by depositing more silver, or some other dense particles, on the existing grains of the image or by replacing some or all of the silver by another material that gives the image a greater optical density. Most intensifiers are salts of heavy metals such as silver, mercury, chromium, or uranium, and a secondary development stage is usually involved in which the metallic complexes formed with the silver of the image are partially or wholly reduced (in the correct sense, this time) to the metals themselves. A typical intensified image might consist, for example, of unchanged silver, metallic mercury, and mercury salts.



In shadow photography, used for fast moving objects, the shadow of the object is cast directly on the film. An electric spark is generally the light source used to cast the shadow, since it is bright, of short duration, and small. Exposures of the order of one millionth of a second may be obtained. The Schlieren method is a development of this and can, for instance, reveal convection streams from heated bodies, vortex rings formed in warm air, or vapours of different densities.
Here, the Schlieren method has been used to show a jet of air issuing from a nozzle, the formation of vortices, and breakdown into turbulence.
Crown Copyright, National Physical Laboratory



Shock waves round a model of a projectile in a wind tunnel, revealed by Schlieren photography. The air flow to which the model is exposed simulates flight at a speed of 6500 m.p.h. The shock waves appear as thin lines, one arising from the nose and the other from the skirt of the projectile.



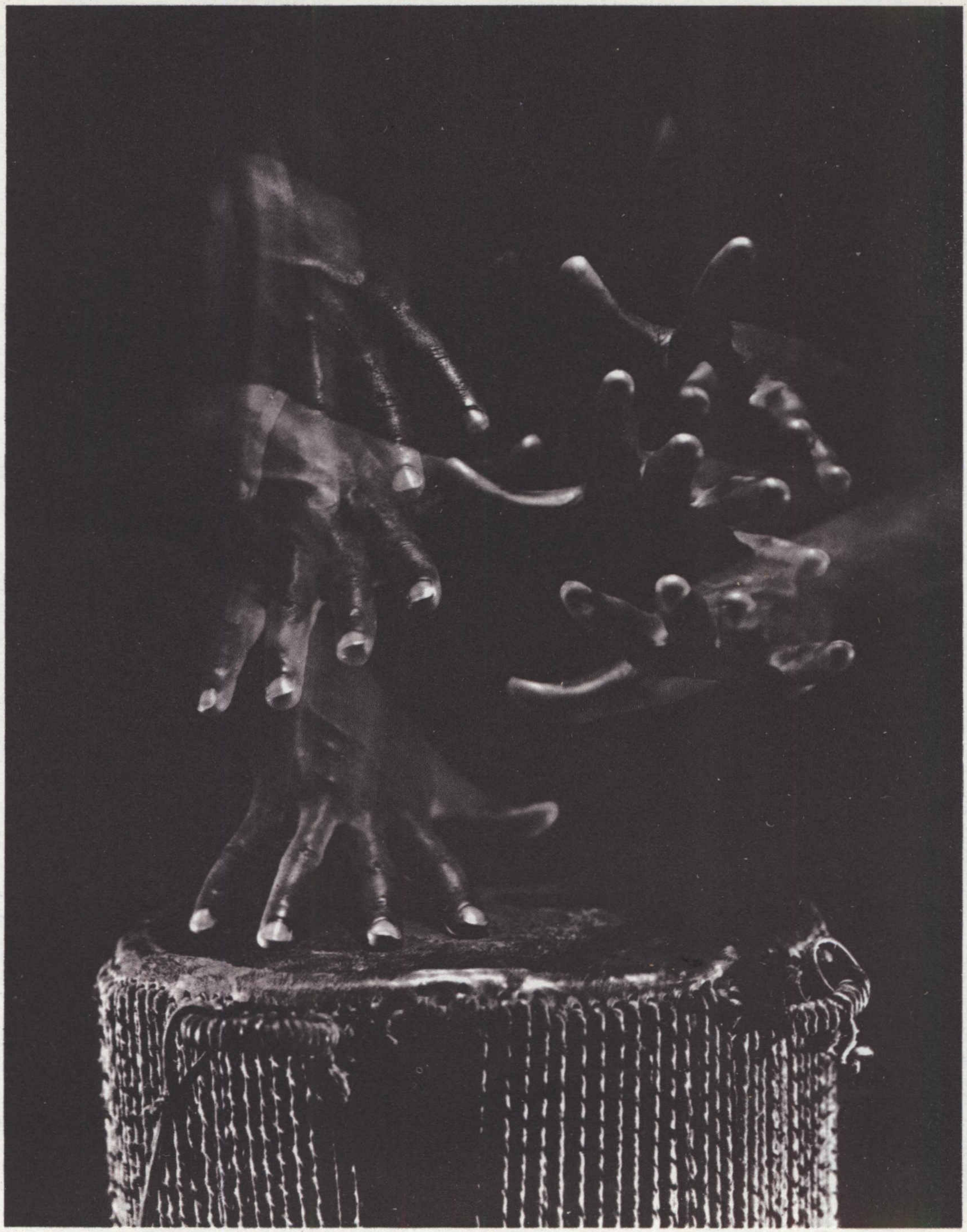
The Schlieren technique is commonly used for photographing shock waves formed in wind tunnels by air streams passing over a model of a projectile. This diagram shows the optical arrangement whereby the waves are photographed. The light is refracted in the wind tunnel by changes in the density of the air near the model. It is then deflected, either onto or away from the cut-off, a small piece of opaque material usually known as the 'Schlieren stop', inserted at the focus of the second mirror. The direction in which it is deflected depends on the nature of the regions of varying density through which it has passed, and areas of the object appear lighter or darker according to whether they cause deflections onto or away from the cut-off.
Crown Copyright, National Physical Laboratory

Toning and colour photography – The normal silver image is more or less black, though the colour of the light it reflects may be affected by the size of the silver particles to give it a brownish or bluish tinge – rather as the smoke from the burning end of a cigarette, which contains myriads of tiny liquid and solid particles, looks blue, while the filtered smoke from the other end looks grey.

Altering the colour of the image by chemical toning – oxidizing the silver to coloured salts – used to be more popular than it is today. The commonest operation, known as sepia toning, was generally carried out by converting the silver to brown silver sulphide. Any sulphide toning that is done nowadays is usually unintentional, arising from inadequate washing and the consequent slow attack on the image silver by residual thiosulphate.

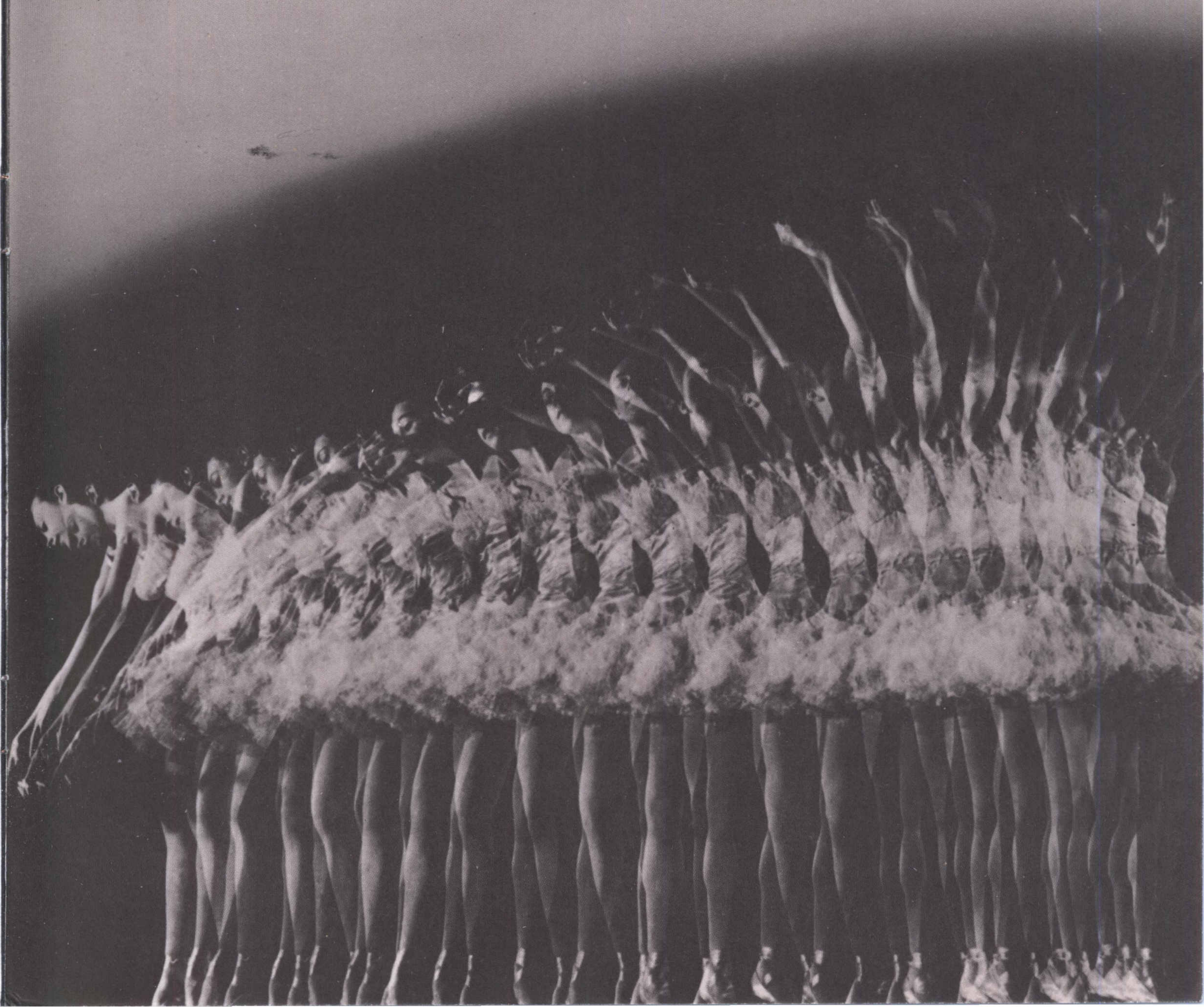
The interesting process known as 'dye-toning' is another matter. The production of coloured images in this way is the basis of most modern colour photography. Practically all colour developers are of the amino type rather than the hydroxy. They couple readily with a great variety of organic compounds called dye-formers or dye-couplers, which are incorporated in the various layers of colour film emulsions or in the formulations used in the different developing stages.

The brilliantly coloured dyestuffs produced by these coupling reactions are deposited at the site of the image and the metallic silver is then bleached away to leave them in all their glory. In some processes an ordinary silver image is first obtained by normal development and is then bleached away; the colours are formed afterwards by further treatment with a dye-forming developer.



A striking example of the photographer's art.
Photograph by George Nicholls. Reproduced from Visual, *published by Ilford Ltd.*

The camera has taken regular glimpses, spaced at short intervals, of the dancer's movements.
Courtesy of Kodak Ltd.



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