

why may not natural selection in unlimited time also cause progressive evolution in directions useful to the organism? I am not ready to say that natural selection is proved as the method *par excellence* of evolution, but I am not ready to abandon it as the most reasonable explanation of evolution until something better supported than the mutation theory is offered as a substitute for it. At the same time the fact should be emphasized that biology has benefited greatly from the investigation and the discussion initiated by the mutation theory. Even though the mutation theory cannot be accepted as a general theory of evolution it has done us great good in dispelling or clarifying the hazy notions which formerly existed as to what natural or artificial, is, as the mutation theory rightly holds, primarily an agency for the elimination of variations, not for their production. It can only act on variations actually existing, and while it can, I believe, continue and extend variation already initiated by shifting in the direction of selection the center of gravity of variation, it cannot initiate new lines of variation. It cannot change a vertebrate into something else nor something else into a vertebrate. It is limited to the modification of existing types of organisms, and to their modification in directions in which they show a tendency spontaneously to vary.

### Discoloration of White Paint

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IN the use of a white "enamel" of good quality trouble was experienced in the tendency of the dried films to undergo discoloration, especially when articles painted with it were stored in a fairly warm situation; under these conditions the whiteness was soon replaced by a yellow or yellowish brown color, the result being much the same whether painted surface was exposed to the light of an ordinary room or was kept in the dark. The enamel or paint normally consisted of an oil varnish mixed with zinc oxide as pigment, and at first the almost natural tendency was to attribute the discoloration to the presence of some impurity in the pigment; as zinc oxide pigment at the present time is also often adulterated with lithopone, consisting mainly of zinc sulphide and barium sulphate, the zinc sulphide in this, by slowly reacting with lead compounds simultaneously present in the pigment or in the oil, might give rise to a gradual discoloration. Although these impurities were found in some samples of the paint, not only did exposure of dried films in an atmosphere of hydrogen sulphide fail to induce a greatly accelerated color change, but samples of similar paint were discovered to be free from lithopone and lead and yet to undergo discoloration in a similar manner. A peculiarity of the discoloration was that it appeared to be confined mainly to the outer surface of the films, the under side against the painted article being affected to a relatively slight extent.

It is an interesting fact that some zinc pigments are not above suspicion as to their fastness; lithopone on exposure to light undergoes a reversible color change, which, however, is hindered by admixture with linseed oil, an extreme and probably exaggerated statement of such behavior having been made many years ago in a description of the behavior of a lithopone paint on certain gate posts, which were "black all day and white all night" (Chemical News, 1881, 43, 282). Zinc oxide, however, is relatively insensitive to light, and the fact that light was not essential to the discoloration now in question disposed of the possibility that the trouble was due to the effect of light either on zinc oxide or on any accompanying lithopone.

Another common cause of the discoloration of white paints, which is often not fully realised, is the ease with which the surface becomes stained with dirt from the external atmosphere, and, among others, H. E. Armstrong and C. A. Klein (Jour. Soc. Chem. Ind., 1913, 329) have drawn attention to the fact that the blackening of white lead paints is frequently due to this cause rather than to the action of atmospheric hydrogen sulphide. In any case the conditions under which the present discoloration occurred rendered this explanation inapplicable.

As the evidence indicated that the source of the discoloration was not in the pigment, attention was turned to the medium, and the seat of the trouble was then located. When a little of the medium was separated from the mixture and was absorbed into paper free from mineral impurities, the dried film, on being kept in a warm place, was found to develop gradually a marked yellowish brown color, a very marked change occurring in a few hours at 60° C. Linseed oil free from "gum," either alone or mixed with pigments, was found to suffer a similar alteration to the oil varnish, but in a still more marked degree.

In order to investigate the change further, strips of paper coated with the white paint, and also with lin-

seed oil only, were hermetically enclosed in glass tubes from which the air had been expelled by a current of carbon dioxide; this gas was generated from marble and recently boiled dilute hydrochloric acid, and was then washed with water and dried with sulphuric acid before use. It was expected that under these conditions the discoloration would be prevented, but the unforeseen result was that the development of the yellow or brown color occurred even more readily. As this color change was effected in the dried paint film in a few hours at 60° C., in an atmosphere of carbon dioxide, the alteration in the oil would appear to be independent, not only of the oxidation to linoxyn, but also of the polymerisation process for which a temperature in the neighborhood of 260°—280° C. is necessary (e. g., see Morrell, Jour. Soc. Chem. Ind., 1915, 105).

Tests were made as to the conditions under which the yellow or brown discoloration could be removed and the original whiteness restored. It is a matter of common knowledge that such bleaching may generally be effected by exposure to sunlight, but for convenience a Cooper-Hewitt mercury vapor lamp was used as a more readily available source of chemically active radiation. In accordance with the natural expectation, it was found that, unlike the discoloration process, the bleaching process required the presence of air or oxygen. When the discolored film, sealed in a glass tube containing carbon dioxide, was exposed to the actinic rays of the mercury lamp the discoloration persisted, although it changed somewhat in tint, becoming a shade browner. Bleached films could again be discolored by keeping in a warm place, and the discoloration and bleaching processes could be repeated many times in succession, the tendency to discoloration then appearing to undergo gradual but only slight diminution. It was not possible to prevent the subsequent occurrence of discoloration in a dried white film by a preliminary prolonged exposure to ultra-violet light with access of air.

During the course of this work the following brief reference to white paints was noted in Lewkowitsch's treatise on "Oils, Fats, and Waxes" (Vol. 3, p. 61): "The paint oil *par excellence* is linseed oil. In the manufacture of high-class white paints for the use of artists cold pressed walnut oil and poppy seed oil are employed in considerable quantities" (see also *ibid.*, Vol. 2, pp. 100 and 125). Although this statement is not definite with respect to any discoloration, it is suggestive of the possibility that white paints made with linseed oil have a less permanent color than similar paints made with the other oils named. Tests showed that poppy seed oil, apart from being paler in color when fresh, certainly has less tendency than linseed oil to discolor in this way, but a distinct, although slower, discoloration was perceptible under comparable conditions, the change in color being still less obvious, although yet distinct, in the presence of a pigment. The especial tendency of linseed oil to discoloration is masked more effectively by white lead than by zinc oxide, doubtless because of the greater covering power of the former pigment, but even with a mixture of white lead and linseed oil the gradual development of the yellow coloration is observable, the possibility of the color change being due to external causes being again excluded by the occurrence of the change in an atmosphere of carbon dioxide in a sealed glass tube. The more feeble covering power of zinc oxide naturally causes the alteration of the color of the medium to be more perceptible.

As to the nature of the chemical change underlying the alteration in color, the experiments now described give no explanation other than that it is apparently independent of the well-known phenomena of oxidation and polymerisation of the oil. Probably some minor ingredient of the oil other than the glyceride mixture which forms the main constituent is to be regarded as the cause of the trouble, but further investigation is necessary before any definite conclusion can be drawn in this direction.—A Paper read before the Birmingham Section of the Soc. of Chem. Ind.

### Cold Work on Copper

At a meeting of the British Institute of Metals a paper was read by Mr. W. E. Atkins describing some experiments on the effect of progressive cold work upon the tensile properties of pure copper.

He remarked that while it has long been known that most metals when submitted to cold work, by hammering, forging, drawing through dies, and so on, have their physical and mechanical properties altered, but few if any attempts have hitherto been made to discover whether any quantitative relationship exists between the amount of cold work done on any metal and the magnitude of the change in its properties. In this experiments a billet of copper was cast and hot-rolled to  $\frac{3}{8}$ -inch diameter in the ordinary way. After rolling

the bolt was annealed for four hours at about 600° C. to ensure removal of the stresses inside the metal, and was allowed to cool slowly. It was then pickled in sulphuric acid to remove external scale, and was cold-drawn by light drafts down to 0.04 inch without further annealing. From the bolt after pickling and from the wire after each draft a few feet were scrapped from the end, and three 2-foot lengths cut for testing. The successive drafts corresponded to the successive sizes of the Imperial Wire Gauge from No. 000000 down to No. 19, or 25 drafts in all. The tensile strength of the wires was determined in the Whitworth laboratories of Manchester University on a 5-ton Buckton machine reading to pounds. Five determinations were made, and these were in every case concordant within 1 per cent; the mean of the five was taken as the actual breaking load, and was converted into tons per square inch.

While the results give a smooth curve for the tensile strength against diameter or sectional area, they at the same time show that the effect of a certain amount of cold work at any stage is intimately connected with the previous history of the metal. Thus there is one stage in the drawing at which a reduction of area of almost 10 per cent (from 0.372 inches to 0.348 inch diameter) is accompanied by no change in tensile strength. The phenomena that present themselves in the drawing of copper are not of the simple nature that might be expected on the amorphous theory. That theory regards the process as continuous, in that further cold work always produces more amorphous material, and therefore gives increased hardness; but the theory, as at present interpreted, offers no explanation of the fact that over a limited range reduction in area by cold working is accompanied by no change in tensile strength. In the absence of quantitative data it appears legitimate to assume that the amount of cold work actually performed on a metal during drawing is measured by the decrease in cross-sectional area; this assumption granted, the necessary conclusion is that two distinct changes, not simultaneous, occur during the cold drawing of copper.

Density, elongation—both general and at fracture—scleroscope hardness, and so on, were all found to change in a similar way to tensile strength. Thus the density becomes constant over a limited range at 8.889, which corresponds to the specific volume 0.11251, the values for the annealed bolt being 8.9165 and 0.11214 respectively. As a tentative explanation the author suggested that the first change is allotropic in nature. After this change is complete, i. e., presumably when the whole of the metal has undergone transformation, a second change sets in, which may be regarded either as allotropic or as explicable on the lines of the amorphous theory; of the two possibilities, the latter appears the more probable.—London Times Engineering Supplement.

### Reduction of the Oxides of Nitrogen to Ammonia Stability of Nitric Oxide

IN Switzerland the conditions are such that oxides of nitrogen can be manufactured more conveniently than ammonia, so that a knowledge of the conditions under which the former are reduced to the latter becomes necessary. The authors have carried out such an investigation, using a special apparatus in which known mixtures of hydrogen with the respective oxides of nitrogen were passed over heated reduced nickel as catalyst. In order to decompose nitric oxide under atmospheric pressure, it is necessary to keep the temperature at or above 575° C. for several hours, even in the presence of spongy platinum as catalyst. Under these conditions, and contrary to what takes place under pressure, there is no formation of nitrous oxide. The primary products of decomposition are nitrogen and oxygen; on cooling, the oxygen reacts with undecomposed nitric oxide to give nitrogen peroxide. Nitrous oxide decomposes into nitrogen and oxygen. In the reduction of nitric and nitrous oxides and nitrogen peroxide by hydrogen, with nickel as catalyst, two reactions take place simultaneously, the one giving ammonia and the other nitrogen. Both in the reduction of nitric oxide and of nitrogen peroxide, the formation of intermediate products (nitrous oxide and nitric oxide respectively), does not occur. Temperatures of 250°–300° C. appear to be the best for the formation of ammonia. Below these temperatures the reduction takes place slowly, while above these temperatures the nickel gradually loses its activity and the ammonia is appreciably decomposed into its elements. Nitric oxide gives the best yields, 70 per cent of the gas on an average being transformed into ammonia; 25–39 per cent of nitrogen peroxide and only 3–7 per cent of nitrous oxide is reduced to ammonia. The reduction of the oxides of nitrogen to ammonia does not, therefore, appear to be of advantage except, perhaps, in the case of nitric oxide, where a more systematic study of the conditions may give better results.—Note in Jour. Soc. Chem. Ind. on a paper by P. A. Guye and F. Schneider, in Helvetica Chimica Acta.