Pigments, Mediums, and Technical Methods of Classical and Mediæval Painters.

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THE subject covered by this title is of vast extent and to give all the sources of information and all the experiments made by myself and others would fill a stout volume. I therefore propose to confine myself to giving results and conclusions and only to deal with sources of information and experimental reasons for certain conclusions at such points as are still open to question or are of especial interest.

To begin with the pigments used in classical times, we have two valuable sources of information, Pliny and Vitruvius, and further we have been able to analyse the pigments found at Pompeii and on the Egyptian paintings. It is evident that at the time when Pliny wrote, a large number of pigments were available for the painter. There were what the artist calls the "earth colours," the red and yellow ochres and terra verte, and the blue and the green carbonate of copper, azurite and malachite, also cinnabar and orpiment, and chalk for a white pigment. In addition to these natural pigments, the two oxides of lead were known, massicot and red lead, and Pliny describes the manufacture of white lead by what was practically the stack process of to-day, and the manufacture of verdigris by the corrosion of copper plates buried in the grape skins from the wine vats. He also describes the precipitation of dyes by means of alum and lye from wood ashes, and tells us that a blue pigment can be obtained from woad and the indigo dye vats, and a pigment derived from the *Murex* shell fish by absorbing the dye in a white earth used for cleaning silver. This may have been an infusorial earth. Although the preparation of mercury from its ores was known, there is no mention of the making of vermilion, which is first described in the Lucca MS., 8th century. For black there were, of course, carbon blacks from charcoal, and lampblack.

In addition the ancients had the blue pigment, made in Egypt, which has been the subject of so much investigation. This blue is a calcium copper silicate which does not occur in nature and is made by an interesting process. Sand is mixed with copper carbonate, lime and a little soda, and kept at a temperature between 800° and 900° for about 24 hours. The whole mass forms a frit in which the crystals of the calcium copper silicate are slowly formed, and the crystals are afterwards separated by grinding and washing. The soda seems to act as a carrier. Below 800° the blue is not formed and above 900° a green glass is obtained, so the temperature has to be carefully regulated for days.* The blue dates from the 6th dynasty and is found on the frescoes at Knossos, and was the universal blue used at the time of Pliny. Somewhere between the second and the seventh century of our era the secret was lost. The furnaces containing cakes of blue have been found buried in the sand of Egypt, and the only known recipe is given by Vitruvius. Until the time of the Ptolemies the Egyptian palette was very limited: carbon black, chalk, red and yellow ochre, Egyptian blue, the green formed by overheating the blue, and malachite.

Although, owing to the uncertainty of the nomenclature, it is impossible to be sure, the production of ultramarine from lapis lazuli does not seem to have been known, though lapis lazuli itself was used as a precious stone. For mediums they had gum acacia, glue, and beeswax. White of egg was used to attach gold leaf, and white or yolk of egg, or a mixture, may have been used as a painting medium, though we have no direct evidence on this point. The use of the drying oils as varnishes or as painting mediums seems to have been unknown. One group of painters used nothing but beeswax, mixed with pigment, either modelling the beeswax with hot bronze tools, or laying on the melted wax, mixed with the pigment, with a brush. Examples of these wax paintings have been found at Hawara in Egypt, in which both methods were used.

As much purely speculative writing on this subject of wax painting is based on the assumption that to paint with pigment mixed with melted wax was impossible, I studied

* *Proc. Roy. Soc.*, 1914, *A*, **89**, 418.

the technique with the assistance of some art students, and we produced pictures which could not be distinguished in appearance from oil paintings.* The difficulty in this climate is due to the rapid cooling of the wax on the surface of the picture. The panel or canvas must be kept warm. As Flinders Petrie has pointed out, in the climate of Egypt the difficulty was the other way, the wax remaining liquid too long.

Wax was also used as a protective medium. The wall paintings in Pompeii were probably done as follows. Layer upon layer of plaster was laid on the walls, each coat before the last was quite dry. The final coat was composed of lime and marble dust, sometimes mixed with pigment, and was brought to a polished surface with the plasterer's trowel. The painting on this surface was probably done with pigment mixed with a little lime or lime water. I have found that a skilled plasterer can produce a surface like polished marble in this way, and that owing to the mass of damp plaster pigments laid on after 24 hours firmly adhere, the painting on plaster freshly laid not being necessary. Finally in some cases wax was driven in by hot braziers. There is no evidence that lime soaps were used as some writers have supposed.

When investigating ancient crafts, we must strictly observe two rules. We must not assume a material or process which is not either found or described, and we must not forget that skill in craftsmanship overcomes the difficulties due to the simplicity of the material.

We have no record of the medium used by the second group of painters whom Pliny mentions.

Turning from Rome and the Roman Empire to Byzantium from the 7th century, we find on illuminated MSS. a red, probably very pure cinnabar, orpiment, malachite, ultramarine from lapis lazuli, and a beautiful crimson pigment probably prepared from *Murex*. Egyptian blue has disappeared. In the Scoto-Irish monasteries, mercury sulphide is replaced by red lead in the earlier MSS. and a pigment prepared from the local shell fish *Purpura capillus*, which is more purple than the pigment from the *Murex*.

A differentiation soon appears in the colour scheme and pigments used on European MSS. on the one hand, and on the Scoto-Irish and Byzantine MSS. on the other. The *Murex* pigment soon disappears from European MSS. and is replaced by a lake corresponding closely to what we call crimson lake. This may have been derived from Brazil wood, kermes or similar cochineal insects, or lac. The recipes for these lakes are very old and I have prepared them all. They are very similar in tint. The lake from kermes is the fastest to light, and Brazil wood lake the most fugitive, but none of them compares in permanence with madder, for which no recipe is given till the 17th century, except an old Egyptian recipe for heating madder root with lime and gypsum, which produces a dull red pigment.

The ultramarine in the early MSS. was very crudely separated from the other minerals in lapis lazuli and while a gradual improvement is seen in the ultramarine on European MSS. the crudely prepared ultramarine was used up to the 12th century on Scoto-Irish MSS., and up to the conquest of Byzantium by the Turks on Byzantine MSS. In fact the palette remained unaltered. The persistence of this older tradition in Irish and Scottish monasteries raises interesting questions as to the origin of Christianity in these Islands and on trade routes.

I cannot leave this early period before 1200 without mentioning two interesting facts. Gold leaf and gold leaf ground as a pigment were of course known from very early times, but on some English MSS. from the 9th to the 10th century I found that gold dust, evidently from river-washed gold, had been used.

Perfectly prepared ultramarine is first found about 1200, and the recipe for its preparation given by Cennino Cennini and other writers is very interesting in the light of our modern methods of ore separation, and the study of emulsions and of surface tension. The finely ground lapis lazuli was mixed with Venice turpentine, a resin, and beeswax, and kneaded from time to time with fingers wet with linseed oil. After some days the mixture was placed in warm water containing a little lye from wood ashes, and kneaded with wooden pestles. The ultramarine separated, leaving the other minerals behind.

* "Greek and Roman Methods of Painting," Camb. Univ. Press.

The cheap blue pigment was apparently always azurite, but deposits were occasionally found so fine in colour that they rivalled ultramarine. The use of azurite occurs on certain illuminated MSS. between 1250 and 1400, and again later. Evidently a very beautiful deposit of azurite was found about 1480, and continued in use to about 1640, when it disappeared from the artist's palette. De Wilde has found it as late as 1660 on one picture only (" The Scientific Examination of Pictures," Martin de Wilde). It was stated to come from Hungary.

The first undoubted example of a madder lake I have identified in the " Speculum Vitae Christi " (18.1.7. Adv. Lib. Edin.), a MS. in the Advocates' Library, Edinburgh, painted between 1460 and 1490. This MS. is also remarkable for having been largely painted with a wax medium, which must have been dissolved in some volatile solvent like oil of turpentine: this therefore is the earliest definite evidence of the use of turpentine as an artist's medium.

Smalt blue first appears about 1600, and the artificial basic carbonates of copper, the blues and greens known as blue and green bice, about 1610—1620, ultimately replacing azurite.

Multitudinous recipes exist for the preparation of blue, green, red, and yellow pigments from vegetable dyes, and from copper. For these I must refer you to Mr. Daniel Thompson's book, " The Materials of Mediæval Painting." Prussian blue appears in the 18th century.

Before leaving the subject of pigments, it is of interest to note that, apart from lakes prepared from dyes, which have only proved permanent in illuminated MSS., the mediæval paint box consisted of minerals; pigments made at a comparatively high temperature, massicot, red lead, Naples yellow (antimony and lead oxide), vermilion; and pigments made by a slow process of corrosion, white lead, and verdigris. These pigments, with the possible exception of red lead, though many of them are quickly destroyed or discoloured by chemical reagents, have proved remarkably permanent throughout the ages. Even verdigris, which has been condemned, is, I believe, more reliable than is supposed. The copper pigments have been condemned for two reasons: being transparent and of poor staining power, they are affected by the yellowing of oil and varnish, and they have been in many instances blackened by the use of alkali and strongly alkaline soaps by restorers. The verdigris used mixed with ultramarine in Watteau's blues is in perfect condition, and the brightest green on a canvas on which oil paints have been painted out, some forty years old, is verdigris. I found on a German MS. of the 11th century (Laing, 5 Ed. Un. Lib.) a copper green which I identified as a copper resinate. The earliest known recipe for such a green is in the De Mayerne MS. (Sloan MS. 2052).

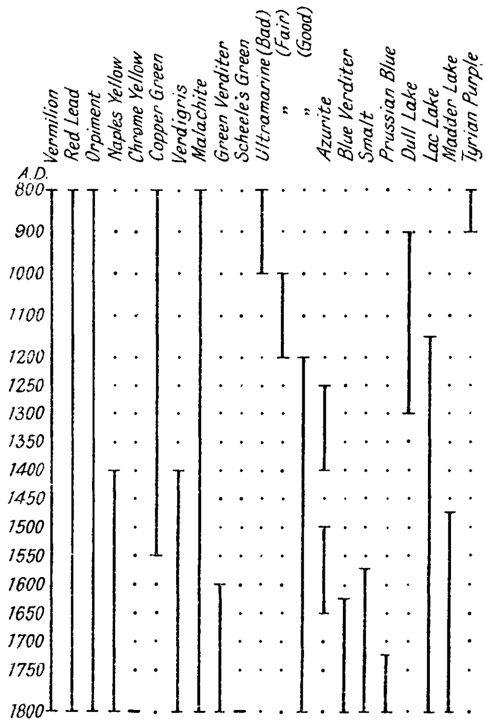

FIG. 1.

Graph showing dates when certain pigments came in and went out.

The yellow lakes used by the Dutch painters have faded, and the red lakes have turned brown and faded, but laid thinly on a bright red background have preserved the richness of colour with which we are familiar.*

* " The Pigments and Mediums of the Old Masters," Macmillan.

Mediums.

Yolk of egg replaces wax as a medium on the Greek ikons after the 6th century,* and is the Italian 13th, 14th, and 15th century medium, being superseded by oil towards the end of the 15th century. It has proved remarkably permanent, retaining its firmness and the freshness of the pigments and resisting organic solvents. We fortunately possess in the book of Cennino Cennini of about 1400 a detailed account of both how to paint in this medium and how to paint in fresco.

The use of drying oils as a medium is described by Theophilus in the 12th century, and the account books of Ely and Westminster of the 13th and 14th centuries show they were the principal medium used in England at that time. Linseed oil, hempseed oil, walnut oil more especially in Italy, and, in the 17th century, poppy oil were used.

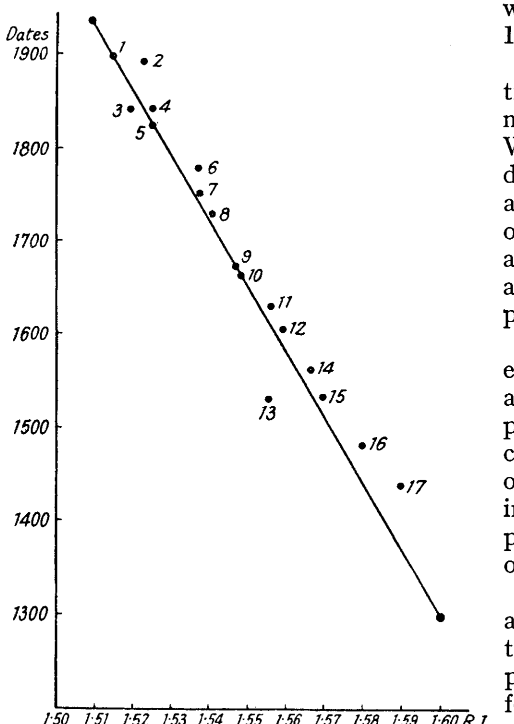

FIG. 2.

We now come to a very interesting question, namely, the technical methods and the medium of the northern 15th-century painters. We have unfortunately no authoritative detailed account of their methods, pigments, and mediums like the book of Cennino Cennini on tempera painting, and must try and arrive at as much knowledge as we can by examination, experiment, and such information as we possess.

There are two problems before us—the extraordinary brilliancy and state of preservation of the early oil paintings, and certain peculiarities of brushwork and technique that continue to the time of Rubens and are more or less present in the Dutch little masters, including Vermeer. Before discussing these problems it is necessary to mention a property of the solid film of the drying oil.

In 1925 a committee consisting of painters and chemists was set up by the Royal Academy to investigate the problems of the modern painter and of the curator. Having no funds for experimental work, it had a short life, but owing to the voluntary work of the chemists on it a little pamphlet was published containing much valuable information which is buried in the archives of the Royal Academy.

One thing had impressed me about modern oil painting and that was the rapid lowering in tone of oil pictures. If a little chrome yellow in oil is spread out and allowed to dry, the dried pigment is already duller and more orange than the pigment in the tube. I asked my friend Dr. Morrell whether it was not possible that the dry linseed oil film kept rising in refractive index as it got older, thus making pigments ground in it more translucent. As no one seemed to know, I bought a refractometer and spread on it a film of linseed oil, which is now ten years old and has never been disturbed. The refractive index rose rapidly at first, then more and more slowly, but is still rising and is to-day 1·512.

Rise in the Refractive Index of the Linseed Oil Film on the Herbert Smith Refractometer.

Days.........	—	1	3	5	8	31	260	865	2700	3885
R.I.	1·480	1·482	1·486	1·492	1·494	1·495	1·500	1·505	1·510	1·512

It is only necessary to examine pigments in liquids of high refractive index to realise how important this is to the oil painter. White lead becomes grey and translucent, and

* I have found on an ikon of about 1700, probably from the Caucasus, a ground of beeswax and yellow ochre, on which the painting was done with beeswax and a drying oil. This revival of an old technique may have been due to the restoration of Christianity in Tiflis at about this time.

FIG. 3.

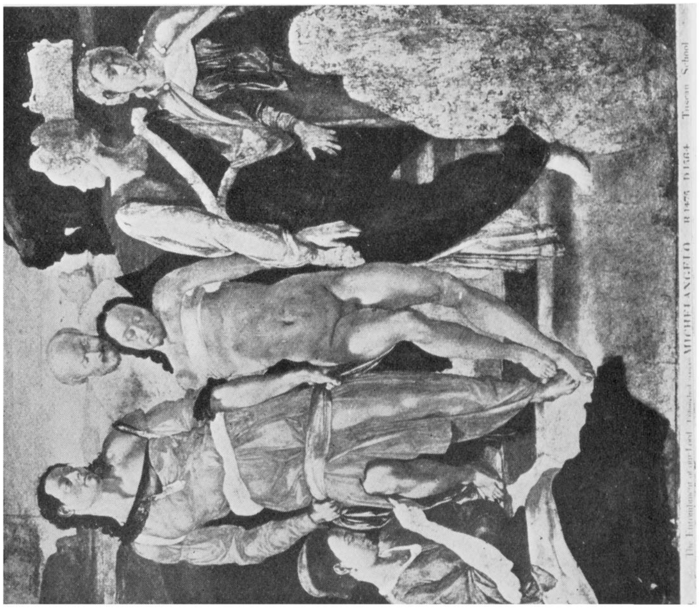

FIG. 5.

[*To face p.* **166.**

Fig. 4.

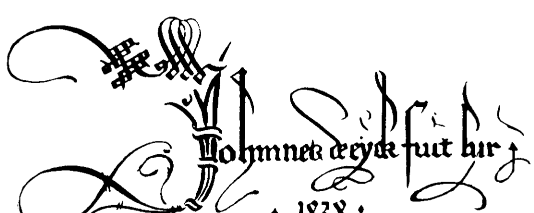

Fig. 6

cadmium yellow and chrome yellow become orange and dull. It seemed of interest to push this matter further and, as many pictures are sent to me to examine, I took to measuring the refractive index of the film of oil by taking a minute sample of the white lead paint, dissolving out the white lead, and measuring the refractive index by an immersion method. I was fortunate early in my experiments to be asked to report on the genuineness of a painted stone statue of 1300, which gave me a starting point of 1·600 R.I. I am publishing the details of these experiments elsewhere.

You will see from Fig. 2 that with occasional irregularities the refractive index of the oil film in old pictures increases with age with marked regularity. Doubtless further researches may reveal exceptions and irregularities, but the general proposition is demonstrated and it accounts among other things for the pentimenti in pictures, and gives us a fresh insight into the technical methods of the early painters in oil.

It is well known that when one oil painting is made over another one, the underpainting ultimately shows through. An interesting example is the appearance of the floor tiles through the dress of the woman standing by the fireplace in the picture by Pieter de Hooch (Nat. Gal. No. 834) (Fig. 3). This increase in translucency must be taking place over the whole surface of oil paintings all the time.

We have enough unfinished pictures of the 15th and early 16th centuries to understand their method. Starting with a surface of gesso, either of gilder's whitening or plaster of Paris which had been mixed with a large volume of water, and glue, the picture was drawn, and either painted in tempera in black, with the gesso for white, or in colour in a tempera medium. On this unchangeable brilliant opaque foundation (egg does not change in refractive index with age) a thin painting of oil colours was laid. As the oil rose in refractive index with age, it became more translucent, and colour and light penetrated more freely through the oil film. Fugitive pigments, such as lakes which fade to a brown, retained their value from the red light reflected from the underpainting. In this way the rise in refractive index of the oil counteracted the dulling caused by yellowing of the oil and fading of pigments.

The unfinished picture by Jan Van Eyck, "The Santa Barbara," in the Antwerp Gallery has been entirely drawn in in black white, and in one corner the blue sky has been laid in in oil (Fig. 4). We have in the Edinburgh National Gallery an unfinished picture, attributed to Cima da Conegliano, complete in tempera, with the oil painting begun on the sky and on the Virgin, and in the National Gallery there are two unfinished pictures by Michelangelo, in which the tempera underpainting has been carried out (Nat. Gal. 790, 809). In 790 the robe of one figure has been laid in in red, ready for the final glazing in oil (Fig. 5).

When this elaborate method was abandoned, the painting was still done on a white priming and the high lights were very thinly painted. Later on, though white lead, very dry and with the minimum of oil, was lumped on for a high light, thin painting on a white ground was continued. To Rubens is attributed the reverse policy, thick painting for high lights and thin painting in the shadows, and Rembrandt reversed the whole technique, but he began on a white ground, on which he thinly scumbled a brown pigment.

It is only necessary to walk quickly through a series of rooms containing pictures of the 15th, 16th, 17th, and 18th centuries to realise that these get darker and lower in tone. Studio tradition had resulted in the sound methods of the 15th-century painters, but of course the scientific reasons were not understood and so it was gradually abandoned. An interesting example of its use is the Rokeby Venus. The background is on a red ochre priming laid over white lead, the Venus on a white priming.

But this is not the whole of the story. There are certain qualities in the paint surface and brushwork of the early painters that cannot be reproduced by raw linseed oil paint, and have led some painters to make the assumption, for which there is no historical evidence, that some kind of emulsion was used. Eastlake sought the solution in the assumption that an oleo-resinous varnish was used. A little varnish was occasionally added to the pigment ground in oil, but there is no evidence of painting entirely in varnish.

Together with the custodian of the gallery in Vienna I was looking the other day at some pictures painted by Rubens himself. We agreed that his medium had qualities which are not possessed by raw oil paint. It was the custodian of the gallery in Edinburgh who challenged me to paint the signature in the Arnolfini picture by Van Eyck in the National Gallery in oil paint : his challenge induced me to take up the question afresh and study again the old recipes. A great deal of attention has been devoted of late years to the study of the polymerisation or condensation products obtained by heating linseed oil, which are known as stand oils. These thickened oils have long been made in Holland, and were used, when prepared by a slightly modified process, for making printer's ink. When used to paint with, they leave a perfectly sharp edge, yet within that edge they flow to form a smooth polished enamel surface. They are remarkably durable, and white lead ground in stand oil remains white while white lead ground in raw oil rapidly becomes yellow. The objection to the theory that they were used by the early oil painters is that they form a sticky medium which, unless thinned with turpentine, no modern painter could use, and the evidence is that turpentine was not used as a medium in the days of Van Eyck.

It seemed nevertheless advisable to look again into the old recipes for preparing linseed oil for painting. To begin with the famous account given by Vasari of what he calls the invention of Van Eyck, he tells us that pigments are ground in walnut or linseed oil, which is their medium, thus disposing of the idea that emulsions and other complex mixtures with wax were used in painting. He also says that Van Eyck *boiled* the oil with certain admixtures of his and that the oil gave a *gloss* of itself without varnish. This might mean the preparation of a stand oil or a drying oil, with litharge, but at any rate the oil was not used raw.

The oldest recipe we have for preparing oils for painting is in the MS. of Eraclius, probably of the 13th century. The oil with the addition of a little lime is to be heated and continually skimmed. When cold it is mixed with white lead and put in the sun for a month or more and frequently stirred. A thickened oil made by this process contains a lime soap. During exposure to the sun an appreciable quantity of white lead is dissolved to form lead soap (Merrifield, Vol. I, p. 232). We thus have a stand oil in which a certain amount of a lead dryer has been introduced by a subsequent process.

The next recipe I shall refer to is the Strasbourg MS. A.VI. No. 19, Public Library, Strasbourg (Eastlake, Vol. I, p. 130). There linseed, hempseed, or old nut oil is to be boiled with skimming with the addition of old bones and pumice stone. I find that, on boiling with bone ash, some 3% of a lime soap is dissolved in the oil. Whether the introduction of lime soap in these oils has any significance is worthy of enquiry. The cold oil is clarified by stirring it with anhydrous zinc sulphate and strained. The author of the recipe says : "The oil will acquire a thick consistence." In this oil pigments are to be ground, and finally a few drops of varnish are to be added.

Messrs. Pearson, who manufacture stand oils, have carried out some interesting experiments on oils boiled in open copper vessels and in copper vessels with a narrow neck. The open vessel gives a stand oil suitable for the painter, the vessel with the narrow neck a stand oil suitable for printing ink. It is to be noted that the development of oil painting and printing went side by side and doubtless the same oil merchants prepared both oils.

Note. Cennino Cennini gives two methods of preparing oil. To make a medium for attaching gold leaf, he boils the oil till reduced to half its volume, and he prepares it for painting by exposing it in a copper bowl till "reduced to half its volume." I have pointed out that the volume would not be reduced in this way, and that the Italian is capable of meaning "till it is bleached." Mr. Daniel Thompson has made a better suggestion, namely, that the oil exposed to the air becomes covered with a thick skin which reduces the volume of liquid oil. A pure cold-pressed linseed oil exposed in an open vessel to sun and air forms a thick skin, and the oil below is very viscous, does not yellow so badly as raw linseed oil, and though not so good as stand oil, has similar properties as a medium. It is possible this was used in Italy. It is interesting to note that this polymerised oil dissolves completely in acetone, thus showing a different polymerisation from that produced by heat.

The question still remains, can a picture be painted with a pigment ground in stand oil? In order to answer it I went to the sign painters, who carry on the old traditions. The sign painter uses a soft brush and a sticky medium. He soaks the oil out of ordinary artists colours with blotting paper and mixes them with a little varnish like those prepared for gilding. He requires a sticky medium to hold the brush. I gave a clever young sign painter some stand oil and a full-sized photograph of the Van Eyck signature and told him to grind lamp black in the oil and copy the signature. The very perfect copy produced shows that it can be reproduced in stand oil (Fig. 6). Stand oil as a medium had exactly the properties he wanted and he was very much interested in Van Eyck's brushwork, recognising in it the qualities that he could get with stand oil alone.

Later on, with the introduction of turpentine towards the end of the 15th century, the use of a stand oil medium became easy. The probability is that artists did not attempt to prepare their own oil, and that, as the demand grew for a freer and more facile handling of oil paint, the oil merchant passed from stand oil to stand oil and raw oil mixtures, very likely adjusted to suit the needs of the painter (Vermeer certainly used a good deal of stand oil), until raw oil alone was used to give the artist the slick medium of to-day which has been the ruin of the permanency of oil painting. The peculiar qualities of surface and brushwork and the remarkable durability of the early oil paintings can be attributed to the method by which the picture was built up on an underpainting upon a white gesso of tempera painting and to the use of the thickened polymerised oils, known as stand oils, in which the pigments were ground.

I have made no attempt here to describe the technical methods required in investigations in which the material is limited to one or two minute particles removed from a picture. For the removal of a particle, either an ordinary hypodermic needle can be used, or a hypodermic needle cut across and ground so as to make a minute cork borer by which a sample is removed, giving a cylinder of paint right through a picture which can be mounted in paraffin wax and cut in sections.

The well-known methods of micro-analysis are available for the identification of pigments, but require modification where only one or two minute and possibly very insoluble particles are available. One method I have found very useful is to dissolve the particle in a small borax bead. Layer after layer can be dissolved off the bead, placed on a glass slide, by successive drops of water, and a separate test applied to each residue (*The Analyst*, 1934, **59**, 246).