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The Russell Effect and its Use in Non-Destructive Testing [and Discussion]

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The Russell effect and its use in non-destructive testing

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The Russell effect was discovered in 1897 when it was found that some types of photographic plate could form an image in the dark when placed in contact with certain organic materials or freshly abraded metals. The technique was largely forgotten for several decades. It is now thought that image formation is due to hydrogen peroxide evolution caused by the autooxidation of the objects under examination. The peroxide reduces the silver halide in the photographic emulsion. Several interesting results have been obtained in the non-destructive testing of materials including the detection of recent abrasions of watermarks, areas of objects exposed to daylight, cracks in paint films and the enhancement of writing. A method for studying the Russell effect with modern materials is described.

Introduction

Some of the most useful methods of non-destructive testing are those which produce an image of the object under examination, e.g. X- and β-radiography, infrared and ultraviolet photography, etc. These methods give an image by using a source of external energy that is modified by the object and subsequently detected, however, there are other methods that do not require any external energy source. For example, autoradiography of minerals uses the fact that some naturally occurring substances are radioactive and will expose a photographic film. Thus, on a flat surface the presence and distribution of certain minerals can be determined.

Becquerel discovered the effects of radioactive substances on photographic film in 1896. A year later, Russell found that certain non-radioactive materials in direct contact with unexposed film could also form images (Russell 1891). Moser in 1842 and de Saint Victor in 1857 (Keenan 1926) had previously made similar observations but, today, the phenomenon bears Russell's name, a reflection of the quantity of work he carried out.

Russell found that certain freshly abraded metals could fog a photographic plate. These metals included zinc, magnesium, cadmium, nickel, aluminium, lead, bismuth and tin. Later he found that certain organic materials would also act in a similar manner. Especially active in this respect were air-drying oils (e.g. linseed oil), woods (figure 2), leaves, most essential oils and natural resins (Russell 1898, 1908). Some workers have found that germanium and silicon will produce images (Ahearn & Law 1956).

Russell found that the active substances were evolving a chemical species that affected the film. He discovered that hydrogen peroxide was able to produce strong images in very low concentrations and therefore concluded that it was produced by oxidation of materials (Russell 1899). Today, this view is almost unchanged but we are now able to reinterpret this phenomenon. It has been established that hydrogen peroxide is evolved from oxidizing metal surfaces in air (Grunberg 1958) and that slow oxidation of organic materials (autooxidation)

Figure 1. W. J. Russell, F.R.S.

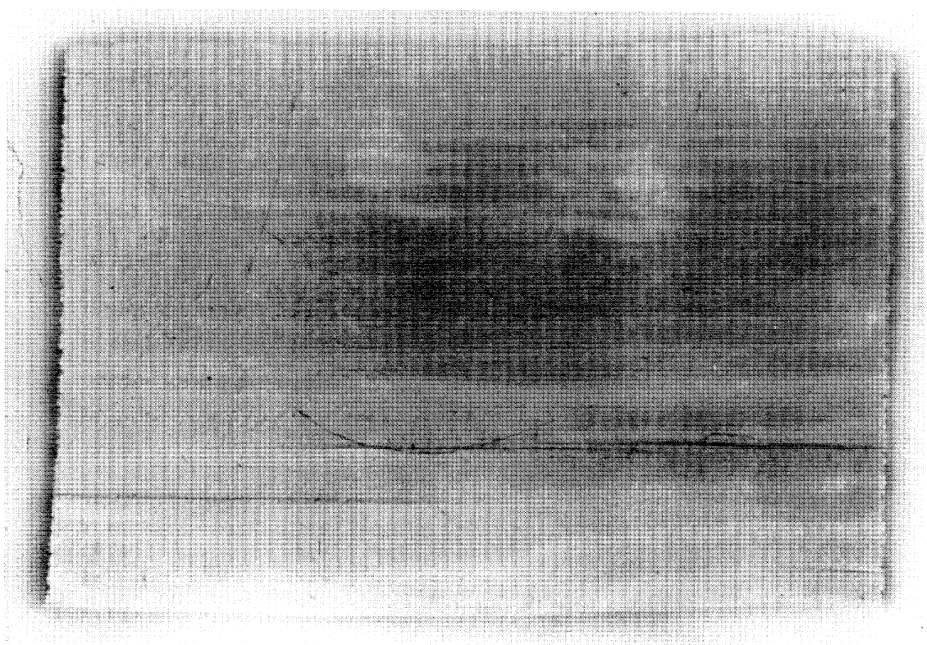

Figure 2. A Russellgraph of a piece of wood.

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proceeds by a free radical mechanism producing an abundance of peroxides, including some hydrogen peroxide.

The formation of hydrogen peroxide during the slow oxidation of phosphorus, oil of turpentine and metals by gaseous oxygen in the presence of water was studied by Schoenbein as early as 1858 (Partington 1961). Since then hydrogen peroxide has been shown to be evolved by a wide range of oxidation processes including oxidation of monosaccharides (Thornally & Stern 1984), phenols, lignin and xylan (Ericson *et al.* 1971) cellulose and primary alcohols (Minor & Sanyer 1971) and propan-2-ol (Ohto *et al.* 1977). In the last study $HO_2^{\cdot}$ was shown to be the chain carrier, this species easily producing hydrogen peroxide by hydrogen abstraction. Indeed, hydrogen peroxide has been prepared industrially by autooxidation of substances such as 2-ethyl anthraquinone (Schumb 1955). Hydrogen peroxide is found in the human body and is produced by plants during photosynthesis (Halliwell & Gutteridge 1925). Other chemicals can produce images on a photographic plate in the same way as hydrogen peroxide, however, it is difficult to ascertain whether the image is produced by the chemical itself or by its oxidation products.

Because hydrogen peroxide is detectable by a photographic plate and because it is evolved by a wide range of objects, the technique has potential as a method of non-destructive testing. This paper will describe how a method has been developed in which photographic film is used to detect the presence of hydrogen peroxide and perhaps other peroxides. Several examples will be given of methods used so far, in the examination of materials.

Production of Russell images

Early workers in this subject were able to use commercially available photographic films, but modern types are not suitable as they are made to be stable to the chemicals evolved by storage materials. A method for studying the Russell effect with modern materials was developed at Kodak's Research Laboratory. Film for the present work was prepared according to the method of Clifford (1975). For the present work, Kodak precision line film FP4 was used. A sheet of film is immersed in 0.05 M ammonium hydroxide for 4 min and allowed to dry. The wet processing can be performed in a darkroom with low level 6 B safelight illumination. Drying of the film takes about 2 h and is done in the dark in a light-tight box.

To obtain a Russell image, flat objects can be placed in direct contact with the film overnight. With thin, flat objects this can conveniently be done inside an X-ray cassette. The film is developed using conventional fixer and developer, in this case Ilford Phenisol and Hypam respectively, each diluted to 20% (by vol) of stock concentration. The mechanism of sensitization to hydrogen peroxide is not clear but may be due to an increase in silver-ion concentration in the photographic emulsion (Jenkins & Farnell 1976).

Image production by hydrogen peroxide is probably brought about by reduction of the silver halide in alkaline conditions, e.g.

$$2AgCl + H_2O_2 + 2OH^- \longrightarrow 2Ag + O_2 + 2Cl^- + 2H_2O.$$

Weak chemiluminescence is known to be produced by oxidation of paper and other organic materials and this method has been used to follow rates of autooxidation (Kelly *et al.* 1979). However, chemiluminescence and phosphorescence can be ruled out as mechanism for formation of images because a piece of silica glass placed between an object and the film blocks all activity.

Applications

(a) *Freshly abraded metals*

Several freshly abraded metals will give a Russell image due to the oxidation of the surface. Thus the technique can be used to detect newly scratched or abraded areas, if a piece of aluminium sheet has been scratched with a steel stylus or partly abraded by using silicon carbide paper, the newly exposed areas show up as dark regions on the photograph. The activity dies away after a day or two. A freshly abraded zinc sheet acts in a similar manner but the activity lasts several days. Figure 3 shows the image obtained from freshly abraded zinc mesh.

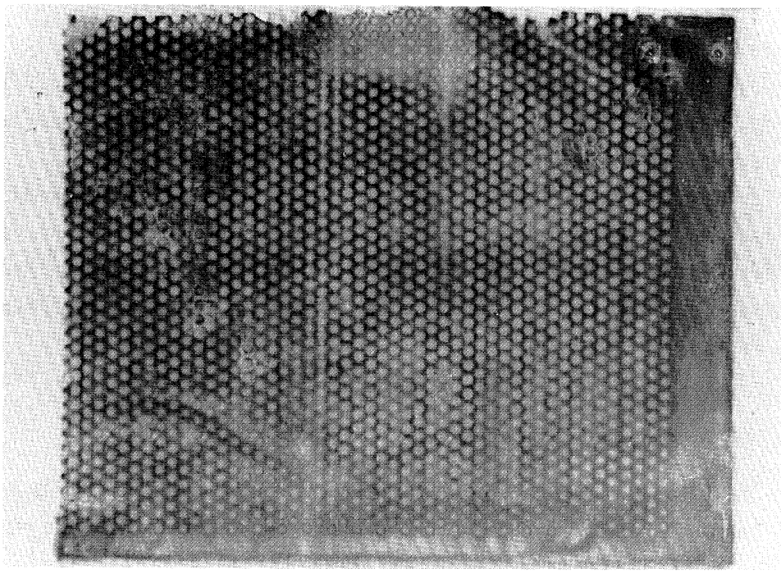

Figure 3. A Russellgraph of a piece of freshly abraded perforated zinc.

If a sheet of aluminium or zinc is abraded over its whole surface it can be used as a source for watermark detection in much the same way as radioactive plastic sheet is used as a source of β-particles. Hydrogen peroxide passes through the paper and its passage is impeded by the printing inks and attenuated by the thickness of the paper. This produces an image of the watermark which is comparable in quality to a β-radiograph. The paper itself also produces an image as it is autooxidizing, but the image due to transmitted peroxides is dominant. Figure 4 shows how the watermark in a Bank of England £5 note can easily be revealed.

(b) *Detection of chemical treatments on paper and other organic materials*

All paper is deteriorating by oxidative processes and will give a Russell image. If the paper has been locally treated with an aqueous solution this invariably produces a change in the activity of the paper by redistributing soluble oxidizing components in the paper or altering the rate of evolution of hydrogen peroxide. The latter process can be changed by either altering the rate of oxidation or trapping or destroying hydrogen peroxide before it can leave the paper. Several organic compounds, such as sodium, aluminium and ammonium sulphates, urea, and sodium carbonate can form addition products with hydrogen peroxide (Schumb 1955), but

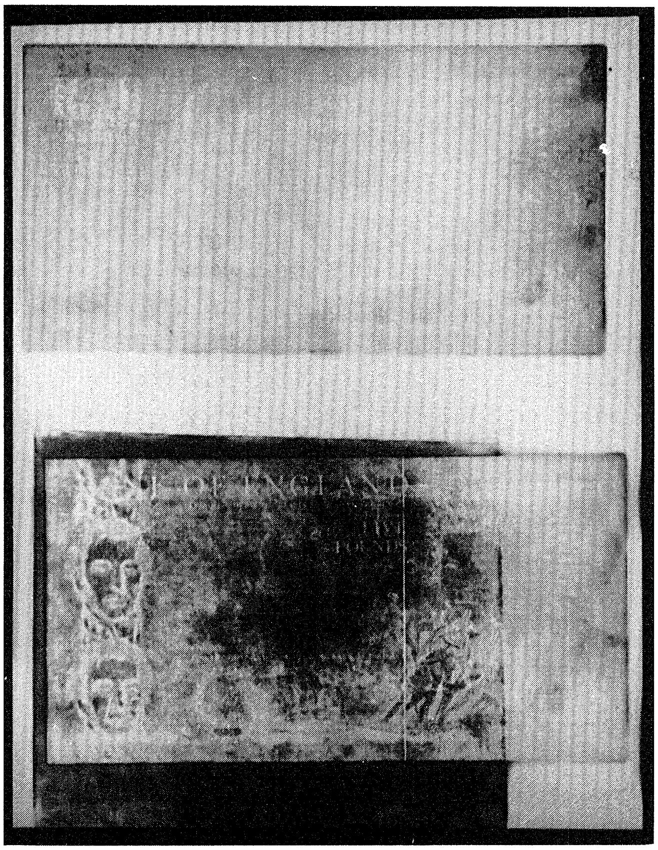

Figure 4. Russellgraph of a Bank of England £5 note (above) and the same with a piece of freshly abraded aluminium behind it revealing the watermark (below).

when impregnated into paper, these chemicals have not been found to alter the Russell image substantially. Iron (II), iron (III) and copper (I) salts can destroy hydrogen peroxide by the Fenton reaction (Halliwell & Gutteridge 1925) and decrease the image produced by the Russell effect, e.g.

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + OH^{\bullet} + OH^-$$

and

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{2+} + O_2^- + H^+.$$

The overall rate of oxidation can be increased but the image produced by the Russell effect is decreased.

When the research work was started it was soon noticed that locally applied aqueous treatments produced an inhomogeneous result in the Russell image of the treated area. This prompted further investigation. When a drop of water is applied to a piece of filter paper it spreads out and eventually dries. Under ultraviolet light the edge of the spot is seen to fluoresce. The Russell image shows intense activity in the fluorescent zone. Both fluorescence and Russell activity decrease over a period of several weeks. The fluorescence phenomenon has been observed on wet–dry boundaries by chemists performing paper chromatography and by textile scientists, and is thought to be due both to movement of soluble impurities towards the edge of the drying spot and to evaporation of the water which somehow enhances the oxidation of substances in the paper (Fox 1965).

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By using the phenomena the Russell effect has a potential use in the examination of suspect documents. In one instance it was noticed, when its Russell effect image was produced, that one piece of paper which had previously been stored in contact with another retained a short-term 'memory' of the other piece.

(*c*) *Testing storage materials*

Storage materials for antiquities should be stable substances which do not give off volatile materials since these may harm objects stored in their vicinity. It is well known that certain materials will evolve organic acids which are harmful to lead, and other materials will evolve hydrogen sulphide which tarnishes polished silver and copper (Blackshaw & Daniels 1977). Hydrogen peroxide is harmful to black and white photographic images because the silver particles which make the image can be oxidized producing yellowing and fading.

McCamy & Pope (1965) discovered that formation of blemishes on microfilm was caused by hydrogen peroxide released by wood, cardboard, paper, paints etc. The blemishes were caused by oxidation of the silver in the photographic image.

In museums, mounting boards for photograph storage are routinely tested for their potential to release hydrogen sulphide. However, previously there was no easy test for hydrogen peroxide evolution, the Russell effect provides a means for performing this test, which is currently undergoing development.

(*d*) *Exposure to light*

It is well known that light accelerates the deterioration of papers containing lignin; for example, newspapers left in the sun rapidly discolour and become brittle. This phenomenon, attributed to photooxidation, can be demonstrated by using the Russell effect. A piece of paper was removed from the inside of a paperback book which had been stored closed. A cardboard mask was made with a star-shaped hole cut in it. The mask was placed over the page and the assemblage exposed to normal laboratory daylight for a few minutes. A Russell image of the partly exposed sheet of paper is seen in figure 5. The areas exposed to light are the star shape at the centre and the top and bottom edges of the page. These show enhanced activity compared with the areas not exposed to light.

The same pattern much reduced in contrast can still be obtained 24 h after the initial exposure to light. As light initiates photooxidation on organic materials some thought must be given to the storage of objects to be examined by the Russell effect as different images may be obtained from an object stored in darkness compared with one stored in daylight.

(*e*) *Enhancement of writing*

Russell reported that he was able to reveal faded writing on paper, as the ink was opaque to the radiation from the paper itself. So far, this has not been investigated in this laboratory, but a related phenomenon has. The writing on palm leaf manuscripts in Burma is produced by scratching the surface of the leaf with a stylus. The leaf has a cellular interior sandwiched between two smooth outer layers. The outer layers are pierced during the writing. As no ink is used in many of the manuscripts the writing can be difficult to see. In the past students have rubbed black pigment into the lettering to enhance it. Figure 6 shows how a Russell photograph shows the lettering clearly. The interior of the leaf appears to have a greater rate of oxidation than the outside and this makes the letters appear darker.

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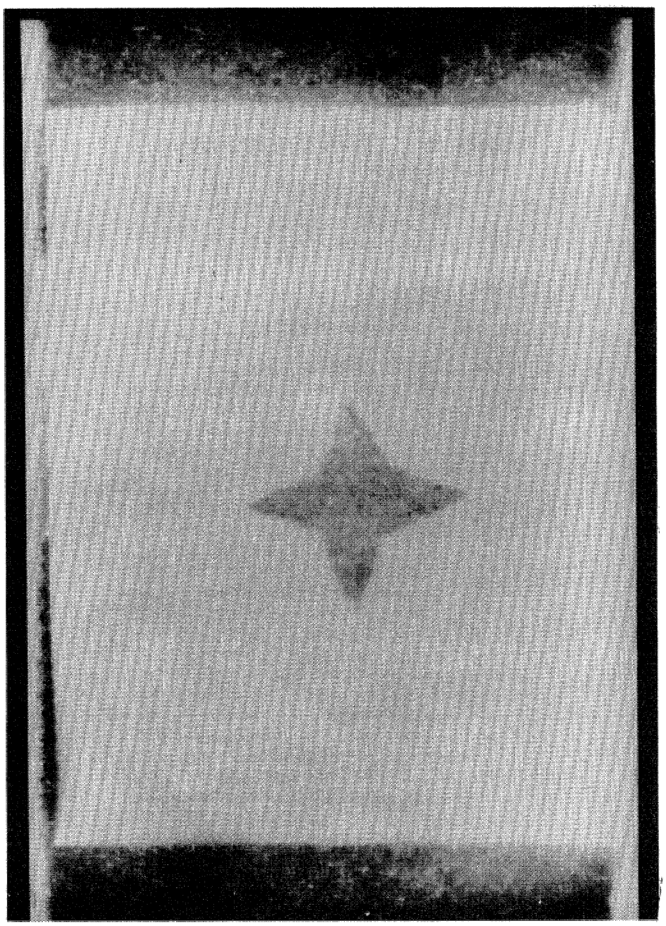

FIGURE 5. A Russellgraph of a piece of paper showing enhanced activity in a star-shaped area that had been exposed to light.

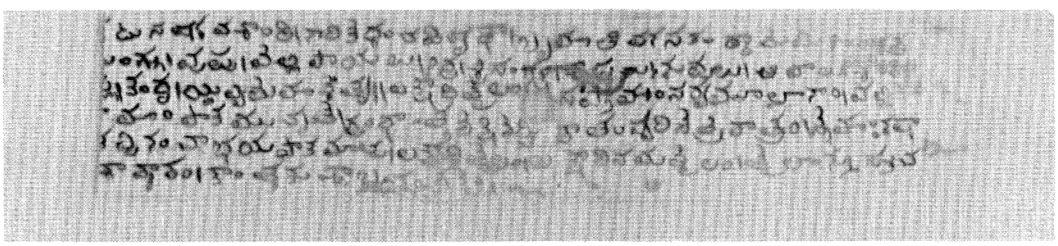

FIGURE 6. A Russellgraph of a palm leaf manuscript showing enhancement of the writing.

(*f*) *Activity of air-drying paints*

Triglycerides containing unsaturated fatty acids are the main constituent of all the popular drying oils, e.g. linseed, poppy and walnut oil. They cure by autooxidation to produce a solid three-dimensional polymer. Newly applied paint films only a few years old can still be oxidizing at a detectable rate. Old paint does not oxidize as fast, if at all, and this difference might be used for detection of recently added paint, e.g. a signature to an oil painting, the newly painted areas standing out blacker than the original paint. Figure 7 shows the picture obtained from

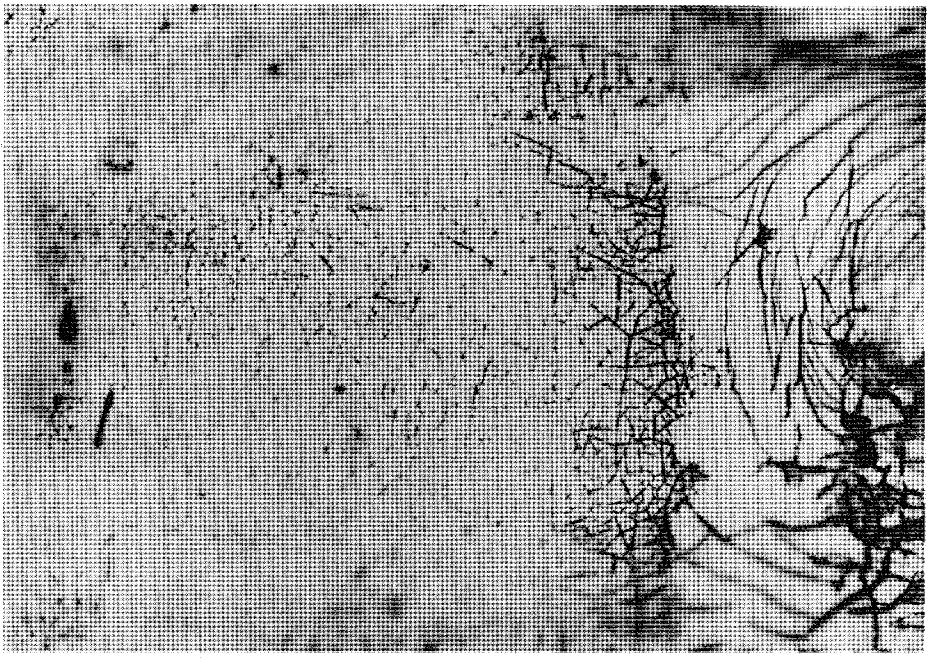

FIGURE 7. A Russellgraph of part of the surface of an oil painting.

an eighteenth-century oil painting. The cracks in the paint varnish layer are easily revealed. In this case no Russell effect is obtainable from the painted image itself.

(*g*) *Other uses for the Russell effect*

Autooxidation is a major cause of deterioration of organic materials and a means of measuring the rate of oxidation is essential to the development of conservation methods aimed at increasing the stability of materials. Previous tests for conservation methods relied on accelerated ageing tests which have an element of unreliability due to the unnatural conditions under which they are carried out. The Russell effect seems to offer an excellent means of monitoring these reactions at room temperature and gives us a new tool to help preserve our heritage.

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Discussion

R. B. Thompson (*Ames Laboratory, Iowa State University, Ames, Iowa, U.S.A.*). The principle of the Russell effect would seem to be appropriate for application to biological systems. Have there been such happenings?

D. V. Daniels. The last few years have seen a surge of interest in the properties and reactions of free radicals in biology and medicine. It has been clearly demonstrated that free radicals are widely found in biological systems, often in oxygen rich enviroments. Thus the Russell effect does seem to have applications in the study of biological systems. However, no work has been performed in this area recently.

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Figure 1. W. J. Russell, F.R.S.

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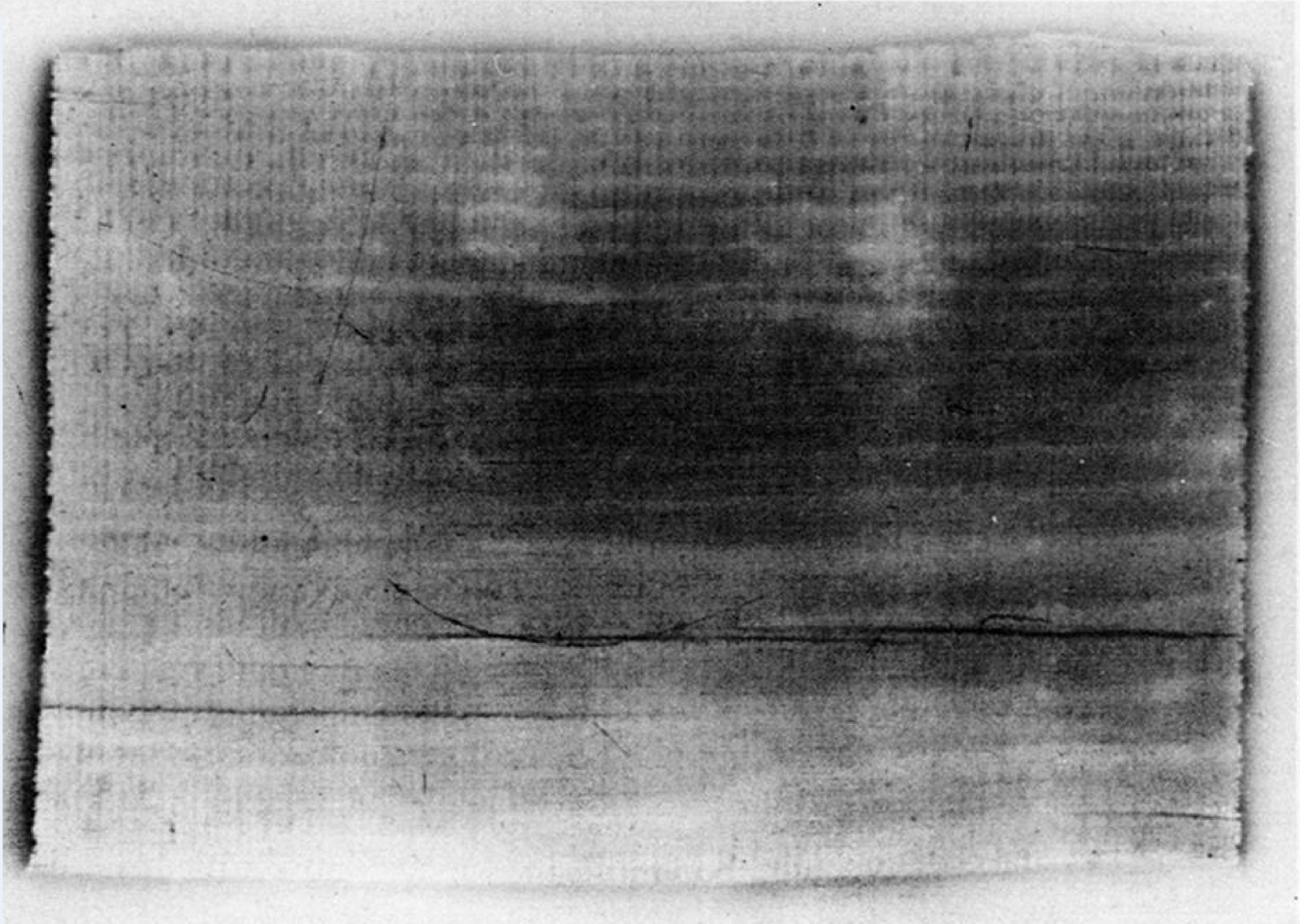

FIGURE 2. A Russellgraph of a piece of wood.

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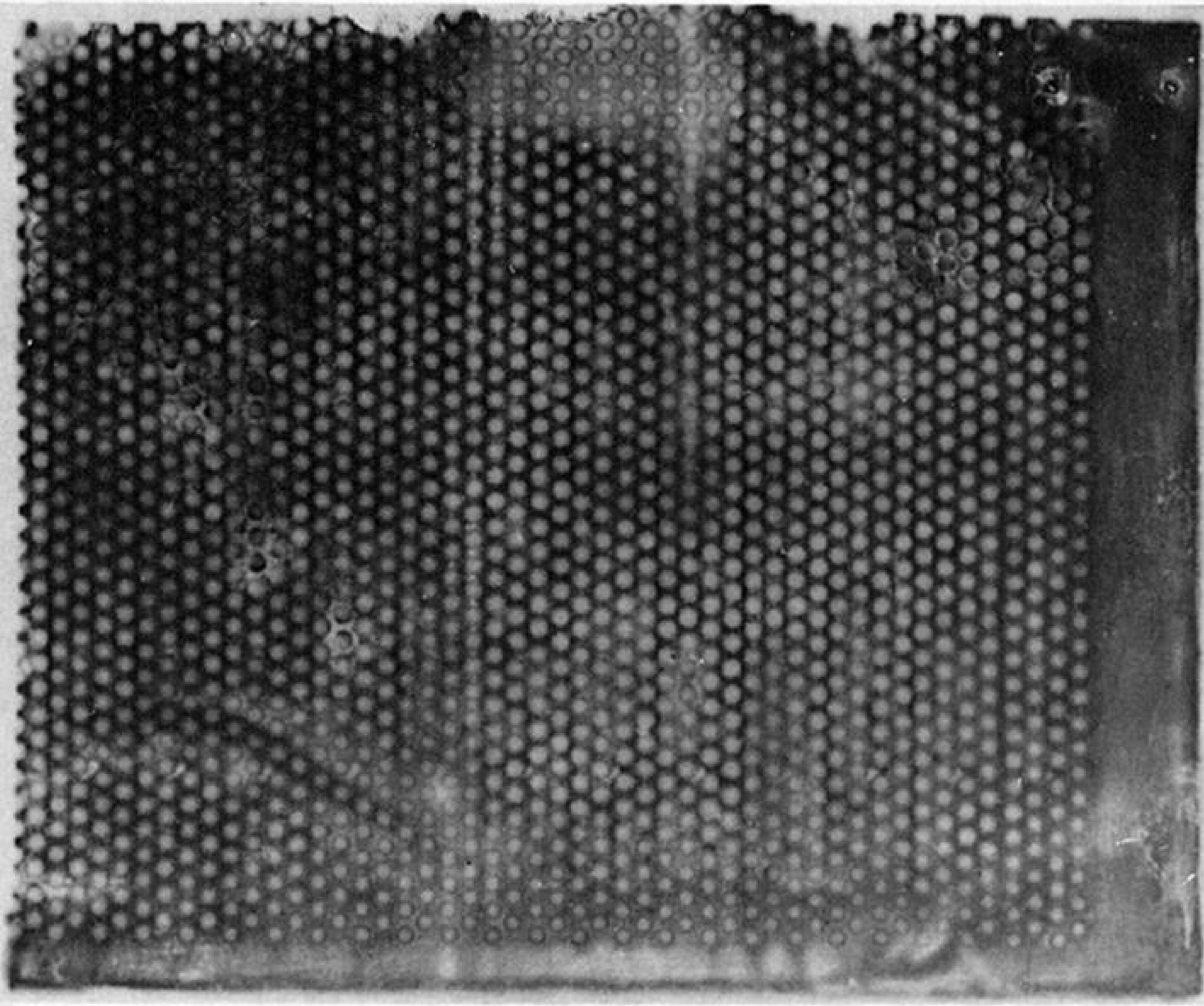

FIGURE 3. A Russellgraph of a piece of freshly abraded perforated zinc.

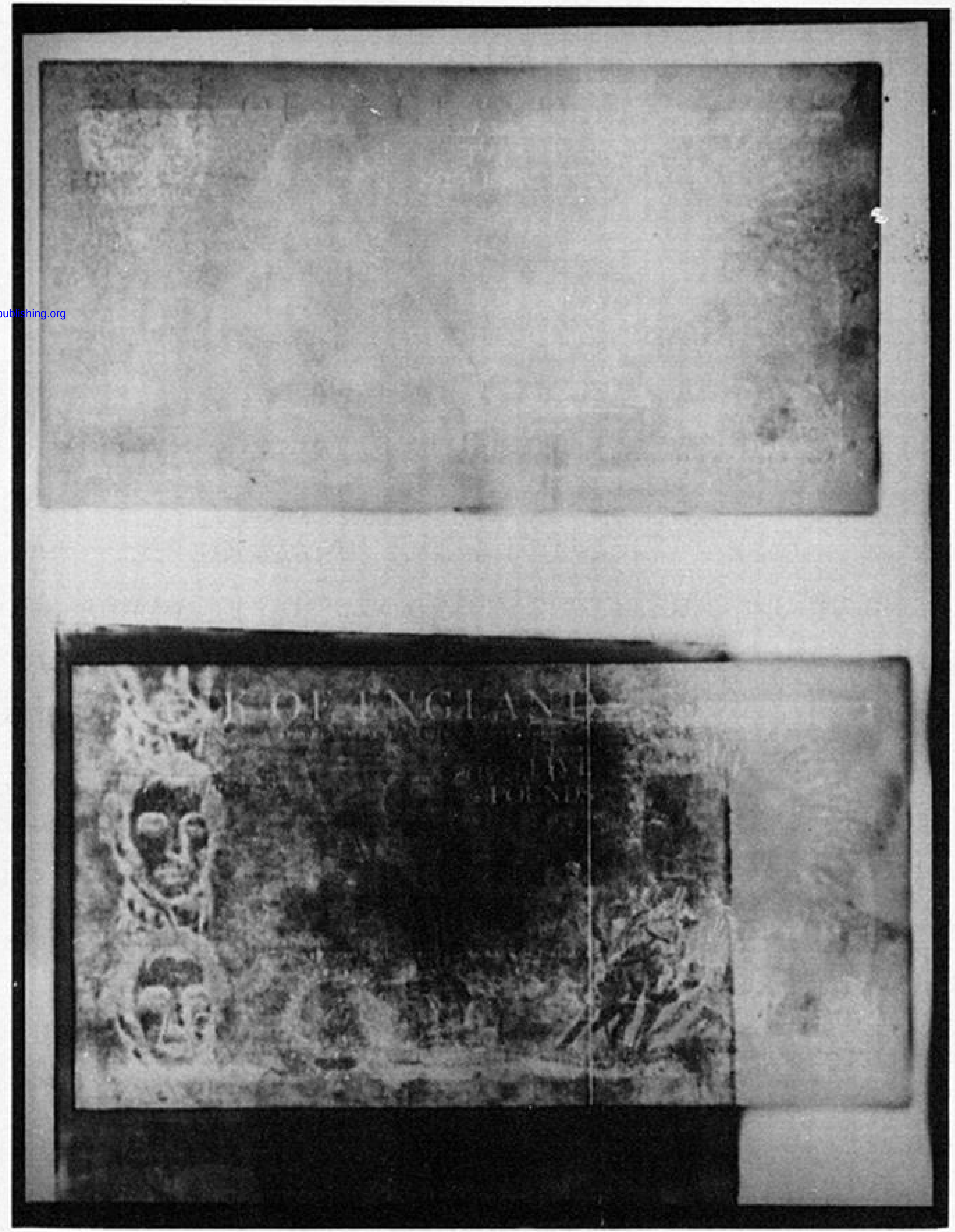

FIGURE 4. Russellgraph of a Bank of England £5 note (above) and the same with a piece of freshly abraded aluminium behind it revealing the watermark (below).

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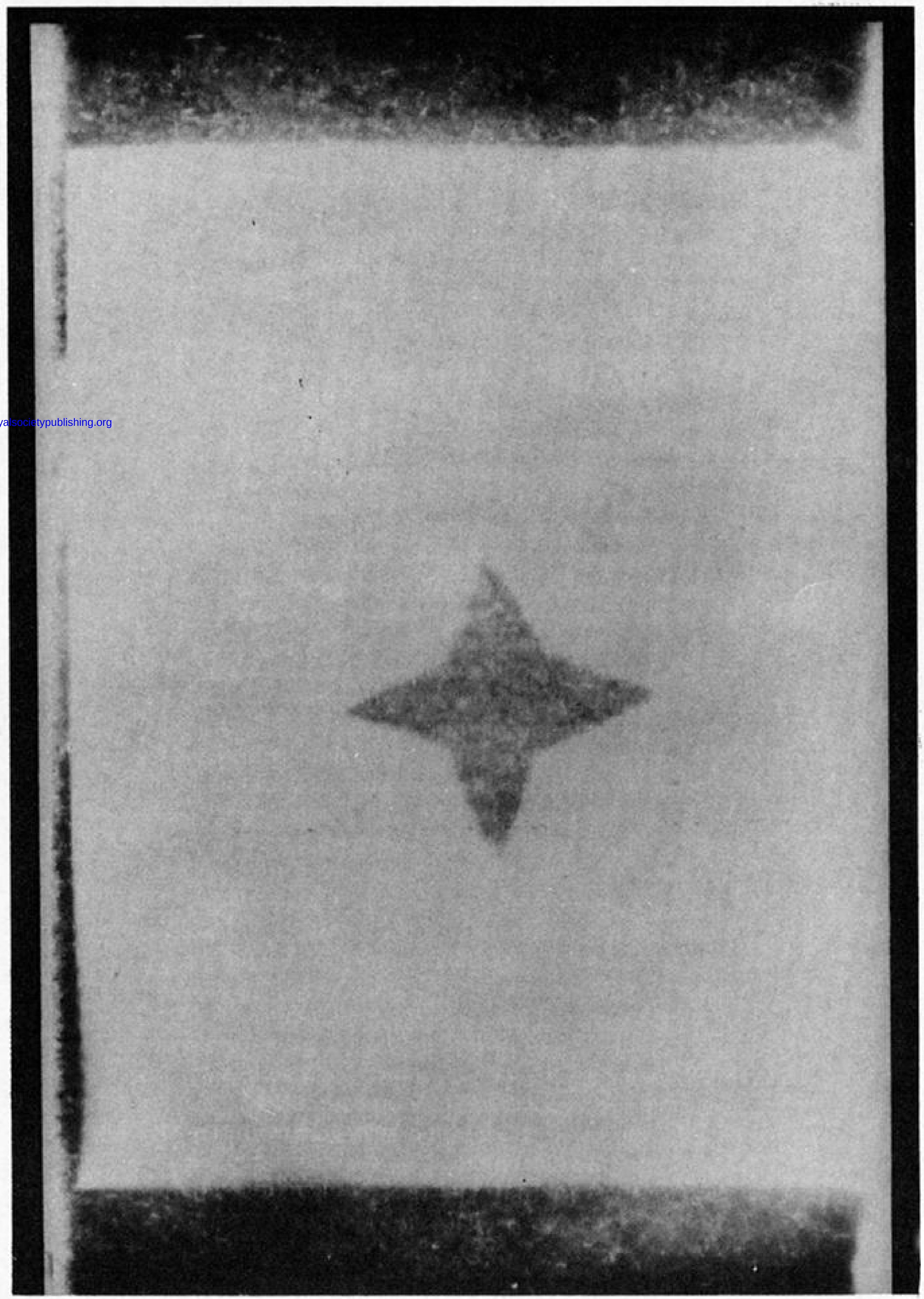

FIGURE 5. A Russellgraph of a piece of paper showing enhanced activity in a star-shaped area that had been exposed to light.

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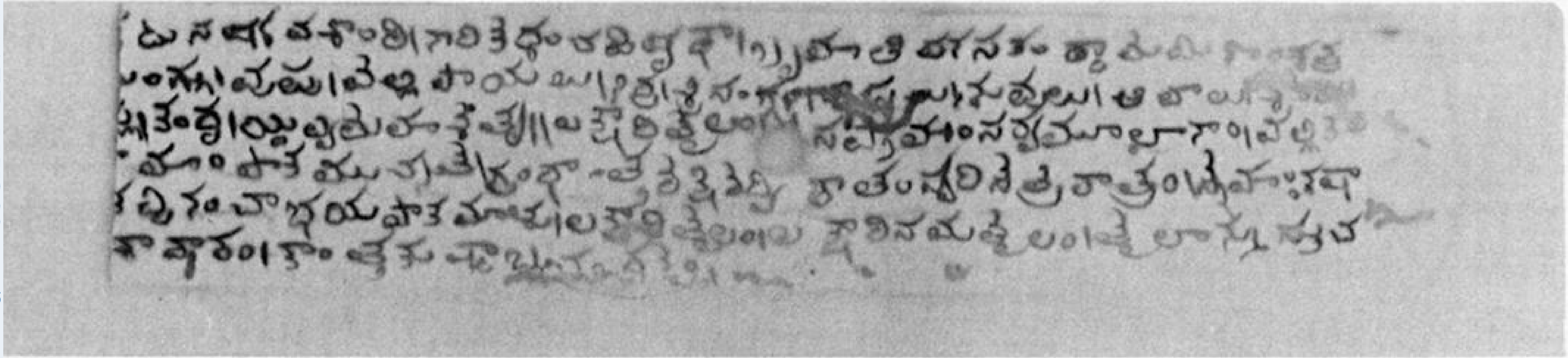

FIGURE 6. A Russellgraph of a palm leaf manuscript showing enhancement of the writing.

FIGURE 7. A Russellgraph of part of the surface of an oil painting.