polymer communications

# An improved permanganic etchant for polyolefines

**R. H. Olley and D. C. Bassett**
*J. J. Thomson Laboratory, University of Reading, Reading RG6 2AF, UK*
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The technique of permanganic etching reveals lamellar detail in polyethylene and other polyolefines allowing representative melt-crystallized morphologies to be studied with the electron microscope. When etching with the original recipe is prolonged artefacts on a scale of $\sim 10\,\mu$m can develop and have probably been misinterpreted as genuine features in some instances. It is emphasized that the conditions of etching should be adjusted to suit the needs of individual specimens. The morphology of artefacts is demonstrated so that they may be recognized as such should they occur. A simple modification of the etchant by incorporating orthophosphoric acid has been found which avoids formation of artefacts on polyethylene.

**Keywords** Permanganic etching; spherulites; electron microscopy; polyethylene; melt-crystallized lamellae; morphology

Permanganic etching, a technique introduced from this laboratory[1], has rapidly proved of great benefit in uncovering the microstructure of melt-crystallized polyolefines. It has been applied especially to reveal representative lamellar organization in polyethylene spherulites grown over a very wide range of conditions, providing details of lamellar geometry to a resolution better than 5 nm[2-5]. This is vital information which has never been available by transmission electron microscopy of polymer samples themselves because of radiation damage[6], but can now be studied by replication (or scanning microscopy) of etched surfaces. Since our initial publication, we in this laboratory have applied permanganic etching to an increasingly wide range of samples which now includes isotactic polystyrene, drawn polyethylene and blends of polyethylene with EPDM elastomers. This has not only demonstrated the versatility of the technique, but continues to develop our confidence that the lamellar structures revealed in etched surfaces are genuine, not least because of extensive cross-checking against thermal and other microscopic techniques where they exist.

It was apparent from the outset, nevertheless, and was pointed out in the original publication[1], that there was some tendency for etching of polyethylene to create artificial structures on a scale of *ca* 10 $\mu$m, which are not part of the sample morphology. Such objects we term *artefacts*. They have been of no consequence in our own work because they are independent of the *lamellar* microstructure which has been our primary concern[1]. If they have occurred in our work, they have been few in number (for the published conditions of etching) and, at high magnifications especially, have not intruded upon regions used for detailed examination. However, under conditions of prolonged etching and more especially for particular concentrations of etchant, artefacts can become numerous and, at optical magnifications, prominent. In some instances we believe other workers have misinterpreted artefacts at low resolutions as spherulites even in, for example, drawn samples, which do not contain spherulites. Clearly one needs to emphasize most strongly that structures which only appear after etching must be regarded with suspicion until their authenticity can be confirmed by knowledge from other techniques.

This communication, which is written in advance of a report of a fuller investigation[7] into the formation of artefacts, has three objectives. Firstly, it is pointed out that the conditions of etching (concentration, time, temperature) can usefully be varied to suit the needs of individual samples and morphologies. Secondly, the appearance of artefacts is described more fully so that they can be recognized should they occur. Thirdly, and most importantly, a simple modification of the etchant, incorporating orthophosphoric acid, is described which in our experience eliminates the formation of artefacts during normal etching of polyethylene.

## *Experimental*

All etching reagents described in this communication are prepared by dissolving a given weight percentage of potassium permanganate in a known volume of acid. This is either concentrated sulphuric acid or a mixture of one or two parts by volume of concentrated sulphuric acid and one part of orthophosphoric acid. The sulphuric acid used is Analar grade (minimum 98%) and the orthophosphoric acid used in the work described here is as received, boiling point 182°C (approximately 92%). In certain circumstances it may be desirable to use dry phosphoric acid (approximately 99%) which can easily be prepared by boiling off water until a boiling point of 250°C is reached. The acid is placed in a conical flask and stirred with a glass covered magnetic stirrer; (PTFE covered stirrers are stained by the reagent.) The potassium permanganate is shaken into the swirling acid, the flask stoppered, and the mixture stirred until all the permanganate is dissolved. The time taken to dissolve the phosphoric acid-containing reagent may be up to one hour. Dissolution of the permanganate is faster if dry phosphoric acid is used

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and the reagent appears to be more stable, especially if etching is continued for many hours; also the possibility of undissolved permanganate crystals remaining is reduced. If the sample has been etched at room temperature it is not necessary to cool it, but at the end of the reaction time it is washed with a mixture of 2 parts by volume of concentrated sulphuric acid and 7 parts of water, which has been cooled to near its freezing point with dry ice. This solution is decanted and the sample is washed successively with hydrogen peroxide (to reduce any manganese dioxide or permanganate present), several changes of distilled water, and finally acetone (or methanol for polymers which might swell in acetone). 2 min is generally an adequate time for each washing. Etched samples have been examined under the electron microscope using a standard two-stage replication process, making a first impression in cellulose acetate and shadowing this first replica with gold-palladium, then depositing a carbon film.

## *Results and Discussion*

The reagent described originally[1] was a 7% w/v solution of potassium permanganate in sulphuric acid. This is the reagent which, used at 60°C, enabled the lamellar morphologies of polyethylene to be characterized[2-5] and is evidently very satisfactory for this purpose. Even so, the need to avoid relaxation of drawn specimens and to obtain more delicate etching of e.g. drawn polyethylene already identified in the original publication[1] led to an extension to other etching conditions. Our experience is that etching at room temperature is generally satisfactory and that a 2% reagent is perhaps marginally better than the initial 7% in revealing lamellar detail in melt-crystallized polyethylene. The appropriate time of etching depends on the individual sample and can be ascertained by examining treated surfaces using Nomarski reflection optics. This technique is a very sensitive monitor of surface topography and, therefore, the formation of artefacts. It shows that artefacts increase in number and size with the time of etching. There are systematic variations with the concentration of the etchant and the distribution is generally uneven, showing a tendency to form along surface scratches, knife-marks or similar irregularities.

It follows that, maintaining other variables as described previously[1], the time of etching for a given concentration and temperature needs to be limited to minimize the production of artefacts. This point is exemplified in *Figure 1*, for a sample of Rigidex 9 polyethylene (BP Chemicals Ltd.) containing both banded spherulites and more granular regions. In *Figure 1a*, etching for 15 min at 60°C with a 7% solution has produced extensive artefacts in the right half of the field. The left half, with many fewer artefacts, would be suitable for detailed study of lamellar textures in banded spherulites. Nevertheless, for this sample, it is obviously desirable to reduce the etching treatment. Suitable conditions are those of *Figure 1b*, namely an 0.2% solution in sulphuric acid at room temperature for 20 h. *Figure 1b* shows some of the very few artefacts produced under these conditions and also both the granular and banded spherulitic textures present.

The structure of the artefacts themselves (which was only glimpsed in the initial paper[1]) is seen in *Figure 2*. This is of the same sample as above, but etched with an 0.7% solution in sulphuric acid for 4 h at room temperature, conditions which produce separate large structures. Although it is quite apparent in *Figures 2* and *1b* that the artefacts are not specifically related to the intrinsic polyethylene morphology which can be seen within them, they do themselves have an appearance suggestive of spherulites. Quite frequently, as on the right of *Figure 2*, the morphology is of centrally connected radiating segments. Just two opposite segments, with a rectangular outline, are not uncommon (*Figure 3b*). Alternatively, as on the left of *Figure 2*, the shapes are rounded, with a tendency to exhibit radial clefts. In profile, artefacts are mostly as seen in *Figure 3a*, though they can be columnar (the extreme left hand structure in *Figure 3a*, out of focus) or undercut, like a mushroom. The variety of plan shapes is exhibited in *Figure 3b*. This refers to a sample of Rigidex 9, crystallized by slow cooling from the melt at 5 K min$^{-1}$ as 0.3 mm thick sheet producing a granular (or microspherulitic) texture. The sample was etched, suspended vertically, in an 0.7% reagent for 4 h at room temperature.

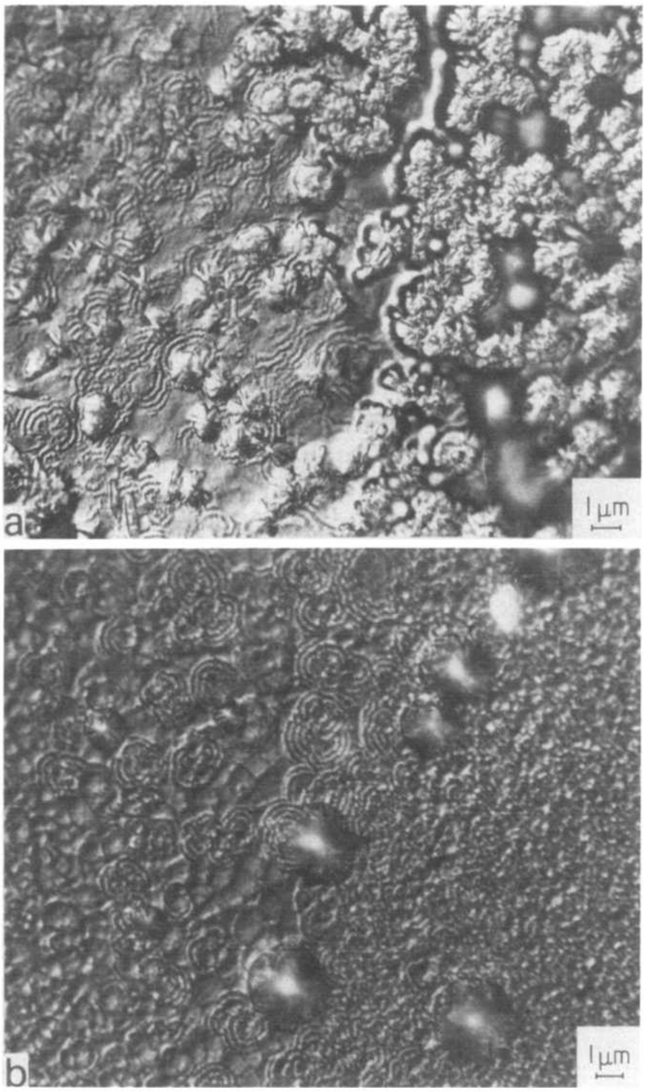

*Figure 1* Artefacts produced (a) densely but unevenly and (b) sparsely with changing etching conditions for a polyethylene sample. The conditions were (a) 7% reagent, 15 min at 60°C, (b) 0.2% reagent, 20 h at room temperature. Note that in both cases the underlying morphology of banded spherulites is unrelated to the artefacts. Nomarski Interference—contrast optics

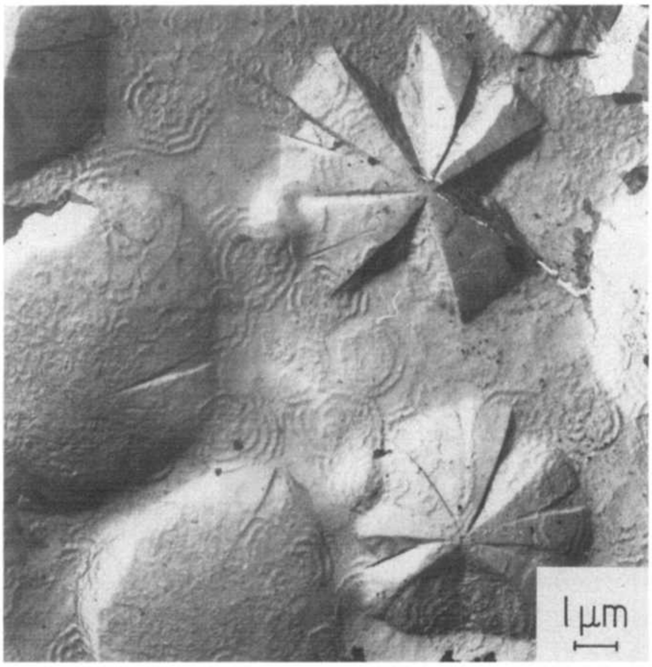

*Figure 2* The morphology of artefacts after etching a polyethylene sample for 4 h at room temperature with an 0.7% reagent. Rings of banded spherulites are visible within the artefacts. Replica viewed by transmission electron microscopy

*Figure 3b* shows the upper part of the specimen; *Figure 3a* is of the top edge of this specimen, of artefacts based on the edge of the sheet. There is a marked increase of size near the top of the specimen; the remaining lower part of the specimen is like the bottom region of the photograph. This variation suggests that the growth of artefacts is linked to convection currents driven by lighter reaction products rising to the surface.

It has, in fact, been shown in a parallel investigation[7] that the cause of artefacts is the precipitation on the polyethylene surface of pinkish brown crystals from the reagent as etching proceeds. The precise nature of the precipitate has not been identified but, from the literature[8], is possibly $Mn_2(SO_4)_3 \cdot H_2SO_4 . 4H_2O$. The presence of these crystals inhibits etching but they are subsequently removed in the washing procedure, leaving the shapes of the artefacts behind in the sample. The nucleation and growth of the precipitated crystals offers a ready explanation of the generally increasing number and decreasing size of artefacts with etchant concentration and their preference for forming on surface irregularities, which is being examined in detail[7].

In addition to the successful applications of permanganic etching to the characterization of representative melt-crystallized morphologies, there has been interest in using the technique to reveal gross spherulitic texture[9–11]. This has to be carried out at comparatively low magnifications where the likelihood of observing artefacts increases. In some instances the structures reported[11] resemble closely the artefacts we have described and additional evidence would be needed to show whether they are indeed genuine features of the sample morphology.

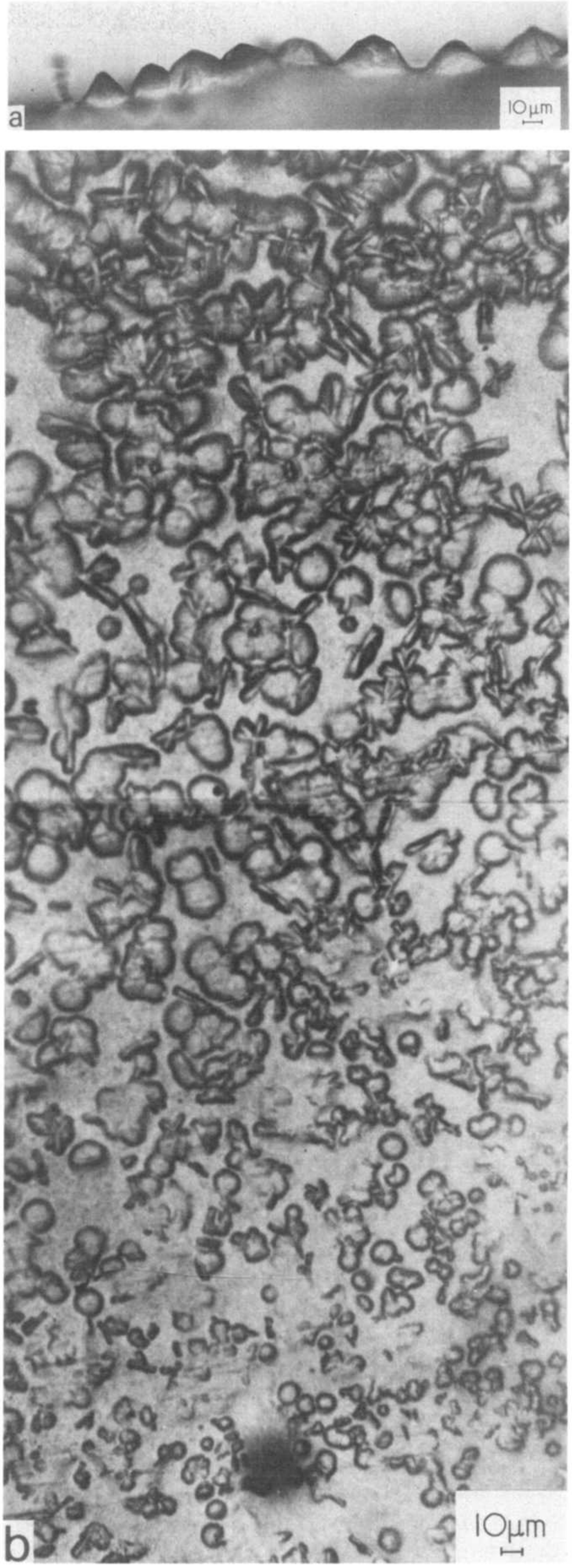

*Figure 3* The shapes of artefacts seen (a) in elevation and (b) in plan in bright field optics, on polyethylene etched for 4 h at room temperature with an 0.7% reagent. The size of artefacts increases towards the top of the specimen in (b) which was suspended vertically during etching. The artefacts in (a) are at the top edge of the specimen in (b)

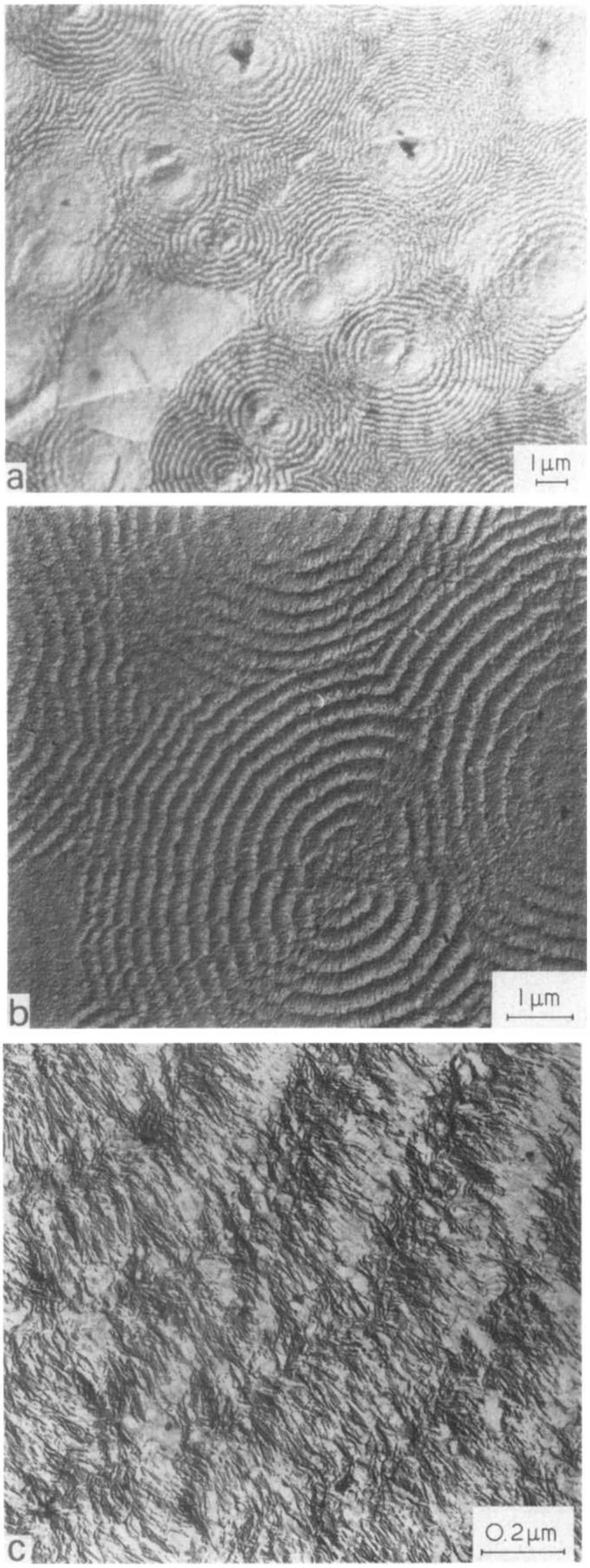

*Figure 4* No artefacts have formed when polyethylene has been etched with an 0.7% reagent in 1:1 sulphuric/orthophosphoric acids for 18 h at room temperature. (a) Nomarski interference contrast optics showing a wide field; (b) details of banding and (c) lamellar morphology are views of a replica examined with the transmission electron microscope

This work of others has brought artefacts into a prominence which they have never had in our own studies. We have, therefore, searched for and found a modification to the etchant which avoids their formation. It is partly to replace sulphuric acid by orthophosphoric. Mixtures of equal volumes or of 1 part orthophosphoric to 2 parts sulphuric acid have proved satisfactory. The acids are mixed and allowed to cool before dissolving the potassium permanganate. Otherwise, the procedure described previously is unchanged.

The effectiveness of incorporating orthophosphoric acid is demonstrated in *Figure 4* for a sample of Sclair 2907 polyethylene (Du Pont Canada Inc.) containing large banded spherulites. The large field of *Figure 4a*, seen with Nomarski interference contrast optics, is free of artefacts as is the entire etched surface. Etching used an 0.7% solution of potassium permanganate in 1:1 orthophosphoric:sulphuric acids at room temperature for 18 h. The addition of the phosphoric acid reduces the rate of etching in general. Replicas of this surface can be examined in the transmission electron microscope at low magnification to reveal details of banding (*Figure 4b*) or at higher magnification to expose lamellar detail (*Figure 4c*).

## *Conclusions*

(1) The lamellar structures observed in polyethylene after permanganic etching are genuine but coarse artefacts, of micron and larger dimensions, develop when etching (to the original recipe) is prolonged. It is desirable to adjust the concentration of etchant and minimize the etching time to suit the nature of particular samples.

(2) These artefacts have probably been mistakenly reported as genuine textural elements in the literature but have characteristic morphological features which help in their identification independently of other evidence.

(3) A means has been found to modify the etchant, by incorporating orthophosphoric acid, which avoids the formation of artefacts.

## *References*

1 Olley, R. H., Hodge, A. M. and Bassett, D. C. *J. Polym. Sci. Polym. Phys. Edn.* 1979, **17**, 627
2 Bassett, D. C. and Hodge, A. M. *Proc. Roy. Soc. A*, 1978, **359**, 121
3 idem, *ibid* 1981, **377**, 25
4 Bassett, D. C., Hodge, A. M. and Olley, R. H. *ibid*, 1981, **377**, 39
5 Bassett, D. C. and Hodge, A. M. *ibid*, 1981, **377**, 61
6 Grubb, D. T. *J. Mater. Sci.* 1974, **9**, 1715
7 Olley, R. H. and Bassett, D. C. (unpublished)
8 Mellor, J. W. 'A Comprehensive Treatise on Inorganic and Theoretical Chemistry', Longmans, 1932, Vol. XII, p 429
9 Barnes, S. R. *Polymer* 1980, **21**, 723
10 Brower, D. V., Naylor, K. L. and Phillips, P. J. Ann. Rep. Conf. Elec. Ins. Diel. Phen. NAS 1980, 113
11 Workshop Proceedings: Morphology of Polyethylene and Cross-linked Polyethylene, EPRI, 1981