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Surface effect of flame treatments on polypropylene

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A study of the effects of flame treatments on a high-impact polypropylene has been performed. Both physico-chemical and mechanical properties have been investigated. The surface chemical composition has been determined by XPS, while the surface tension and the polarity were obtained through contact angle measurements. A remarkable agreement in the behaviour of chemical composition and polarity has been found, emphasizing the role of carbonyl and carboxyl groups. The adhesion of treated and untreated samples to paint coatings has been mechanically tested. The force of adhesion remains quite constant after the first flame treatment. This suggests the importance of chemical interactions of the coating with the first layers of the polymer.

1. Introduction

It is well known that thermoplastic polyolefins (TPO) show poor adhesion with all other materials. This behaviour can be explained by both the absence of polar or reactive groups in these polymers and by their solvent resistance. A number of treatments have been applied to TPO in order to improve their adhesion to inks, paint coatings, etc. The effect on the surface composition of irradiation methods [1-6], electron bombardment [7] and electric discharge treatments [8, 9] were investigated to understand the chemical origin of the improved adhesion.

Flame treatments have often been used on TPO, but little is known about their effect on the surface of polypropylene. This paper presents the results of a study of the effects of the flame treatment on high-impact polypropylene. A study on polyethylene has been previously reported [10].

2. Experimental details

2.1. Materials and sample preparation

In a first series of experiments, different commercial high-impact polypropylenes were flame treated. As expected it was found that the ethylene-propylene rubber (EPR) content increased the surface reactivity of polypropylene, even if the reaction mechanism should be considered quite independent from the composition.

After this step, a high-impact material was selected for the present study because it was currently painted on industrial scale after flame treatment. Plaques (20 cm × 7 cm × 0.3 cm) were injection moulded at 250° C using a Plastinjector GBF 90 injection machine. The flame treatment was performed by placing the plaques on a conveyor-belt running at constant speed under a linear burner supplied by Samia SpA. The flame was obtained by the combustion of a propane-air mixture. The temperatures in the flame were 1200 and 1040° C, at 2 and 4 cm from the burner, respectively.

The flame equipment allowed the use of different speeds for passing the specimen under the flame. The range was 1 to 30 $\mathrm{m\,min^{-1}}$ (resulting in different treatment times). The distances from the burner were varied in the range 1 to 6 cm.

2.2. Analysis

X-ray photoelectron spectroscopy (XPS) spectra were obtained on a PHI model 548 XPS-AES spectrometer, using the Mg$K\alpha$ radiation (1253.6 eV) from a 400 W source. The analysis chamber pressure was maintained near 2×10^{-7} Pa, without baking.

Signal averaging to obtain good spectra was possible due to the connection of the spectrometer to a PDP 11/50 computer. Further data processing (smoothing, background substraction, integration, deconvolution) was carried out using in-house software on a Sperry 1100/72 mainframe computer.

The hydrocarbon C1s peak was used as a reference and set to 284.6 eV. The surface composition was calculated from the spectra using the appropriate sensitivity factors [11].

Contact angle measurements were carried out using an internally developed apparatus. The measurements were obtained by the direct observation of the angle formed by the tangent to the drop with the surface.

H_2O and CH_2I_2 were used to obtain contact angles. The Harmonic Mean equation [12] allowed us to

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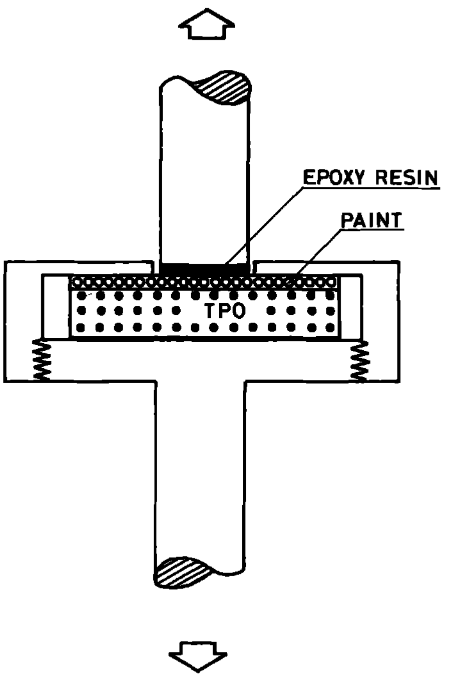

Figure 1 Adhesion-force test for paints. The stress is applied perpendicular tó the polymer/paint coating interface by a tensile equipment and the observed maximum load is the adhesion force of the paint layer.

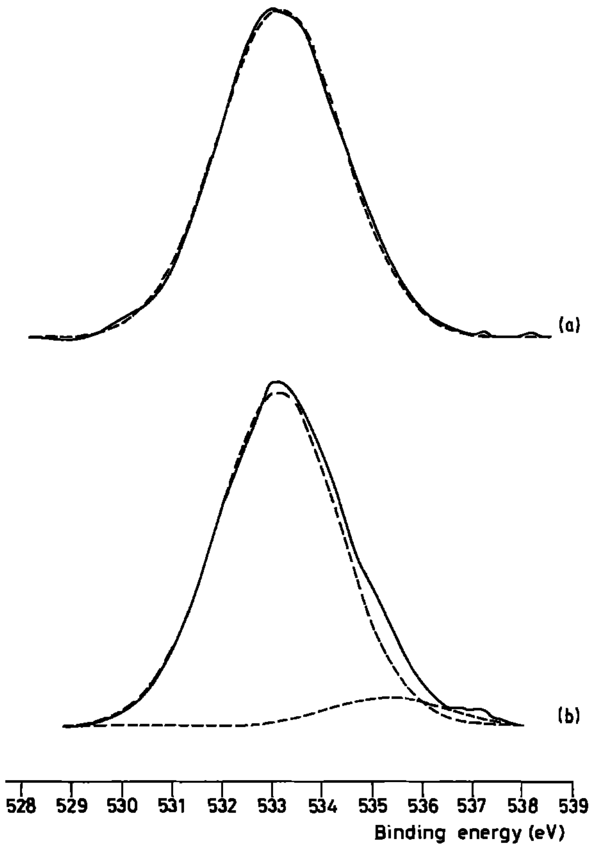

Figure 2 XPS Cls spectra of flame-treated polypropylene; (a) one treatment, (b) four treatments.

obtain for each sample the surface tension (Γ) and its polarity (Γ*p*) for each sample [13]. A homogeneous surface was assumed.

The estimated error in the contact angle measurement is 2 to 3 deg. This corresponds to a margin of error of approximately 1 to $1.5 \times 10^{-5}\,\mathrm{N\,m^{-1}}$ in the value of surface tension and 0.01 to 0.02 in the calculation of polarity.

Adhesion of the flamed surface to paint coatings was also measured. Plaques of treated and untreated polypropylene were painted by spray gun with commercial two-components systems of polyacrylic-polyester and polyurethane paints.

The adhesion test was performed by measuring the maximum force required for debonding of the paint layer. To this purpose a steel cylinder was stuck on the surface of the coating by epoxy resin and the tensile test was carried out by the anular support outlined in Fig. 1. In our opinion, this test (as compared to others, i.e. peeling) should be less sensitive to the mechanical characteristics of the materials.

2.3. XPS

As expected, XPS spectra allowed us to detect essentially carbon and oxygen on the surface. We also found a variable amount of silicon on our surfaces. It can be attributed either to the appearance at the surface of some mineral filler, or to a limited contamination of the surface by silicon grease, very often introduced on polymer surfaces in printing processes.

TABLE I Surface composition of polypropylene samples

Sample	%C	%O	%Si
Untreated	97.7	2.3	–
1 Tr. ($15\,\mathrm{m\,min^{-1}}$, 4 cm)	90.2	9.1	0.7
2 Tr. ($15\,\mathrm{m\,min^{-1}}$, 4 cm)	86.8	12.8	0.4
3 Tr. ($15\,\mathrm{m\,min^{-1}}$, 4 cm)	76.3	19.1	4.6
4 Tr. ($15\,\mathrm{m\,min^{-1}}$, 4 cm)	82.8	15.3	1.9
1 Tr. ($15\,\mathrm{m\,min^{-1}}$, 2 cm)	88.0	11.4	0.6
1 Tr. ($5\,\mathrm{m\,min^{-1}}$, 4 cm)	86.8	12.1	1.1

In Table I the atomic percentages of carbon, oxygen and silicon relative to the samples we examined are displayed. An overall increase in the amount of oxygen with the number of flame treatments has been observed. It should be kept in mind that part of the oxygen is due to mineral filler and contaminants, so from the oxygen percentage an amount roughly equal to the silicon percentage (assuming the silicon grease contribution is dominant) should be subtracted to obtain an estimate of the amount of oxygen actually bonded to carbon and, as such, introduced by the frame treatments.

The deconvolution of Cls spectra revealed the presence of three to four contributions. In Fig. 2 the carbon spectra relative to one (bottom) and four (top) flame treatments are displayed with the corresponding components (dotted curves). Consideration of the relative binding energies prompted us to assign them tentatively to the following functions [4]: (1) carbon bonded to hydrogen or carbon (B.E. 284.6 eV); (2) carbon singly bonded to oxygen (B.E. 285.8 to 286.0 eV); (3) carbonyl (B.E. 287.5 to 287.7 eV); (4) carboxyl (B.E. 289.9 to 289.2 eV). The relevant data are shown in Table II.

The total amount of oxygen bonded carbon is reasonably proportional to the amount of oxygen, particularly when the oxygen percentage is freed from

TABLE II Results of curve fitting of Cls photoemission peaks

Sample	B.E. (eV)	rel. %	at. %
Untreated	284.6	95.6	93.4
	285.9	4.4	4.3
1 Treatment	284.6	79.3	71.5
15 m min^{-1}	285.9	16.6	15.0
4 cm from the burner	287.6	4.1	3.7
2 Treatment	284.6	73.5	63.8
15 m min^{-1}	285.8	19.1	16.6
4 cm from the burner	287.7	7.4	6.4
3 Treatment	284.6	67.0	51.1
15 m min^{-1}	285.9	24.7	18.8
4 cm from the burner	287.5	6.5	5.0
	289.0	1.8	1.4
4 Treatment	284.6	67.2	55.6
15 m min^{-1}	285.9	24.8	20.5
4 cm from the burner	287.7	6.1	5.1
	289.2	1.9	1.6
1 Treatment	284.6	74.2	65.3
15 m min^{-1}	285.9	19.6	17.2
2 cm from the burner	287.7	6.2	5.5
1 Treatment	284.6	74.6	64.8
5 m min^{-1}	286.0	19.3	16.8
4 cm from the burner	287.7	6.1	5.3

silicon grease contributions. An interesting feature of these spectra is the constant increase of carbon singly bonded to oxygen with the number or harshness of flame treatments. At the same time the presumed carbonyl contribution (binding energy around 288.5 eV) is increasingly important up to two flame treatments, decreasing slightly with the subsequent treatments. The third and fourth flame treatments originate a certain number of carboxyl groups.

All these observations are summarized in Fig. 3. It can also be noted how the "harsh" treatments (less distance between the flame and the sample, or slower passage) produce a situation intermediate to those corresponding to one and two "normal" treatments.

Oxygen spectra are for far the less informative. As previously reported [10], in polymers a similar binding energy is often observed for oxygen atoms in different chemical environments, with the exception of CO(O)R oxygen atoms. In Fig. 4 oxygen spectra relative to one (bottom) and four (top) flame treatments are displayed. When the carboxyl function is detected in carbon spectra, a second contribution is also seen in oxygen spectra, some 1.8 to 2.0 eV higher in binding energy than the principal peak.

TABLE III Surface tension and polarity of polypropylene samples

Sample	Surface Tension (10^{-5} N m^{-1})	Polarity
Untreated	28.0	0.136
1 Tr. (15 m min^{-1}, 4 cm)	42.7	0.354
2 Tr. (15 m min^{-1}, 4 cm)	43.4	0.391
3 Tr. (15 m min^{-1}, 4 cm)	43.8	0.340
4 Tr. (15 m min^{-1}, 4 cm)	40.3	0.343
1 Tr. (15 m min^{-1}, 2 cm)	40.7	0.360
1 Tr. (5 m min^{-1}, 4 cm)	41.6	0.366

Unfortunately our equipment was not suitable to perform variable-angle XPS experiments. Thus it was not possible to measure the thickness of the oxidated layer as a function of the treatment. The thickness of material examined by XPS is a function of electron mean free path. In our case we analysed approximately 3 to 5 nm of material.

2.4. Surface tension and polarity

Contact angles of different liquids on the surfaces of our samples were measured in an attempt to correlate the thermodynamic properties to the chemical composition. In Table III the results of this analysis are shown.

Steinhauser and Ellinghorst [9] reported the contact angles of water on electric (corona) discharge treated polypropylene, which are comparable to those found in flame-treated samples.

The surface tension arises from various contributions relative to different interactions. Among these, important are Van der Waals forces, dipole–dipole interactions and hydrogen bonds [13]. The polarity of the surface is defined as the fraction of surface tension that can be attributed to polar interactions (dipole–dipole interactions and hydrogen

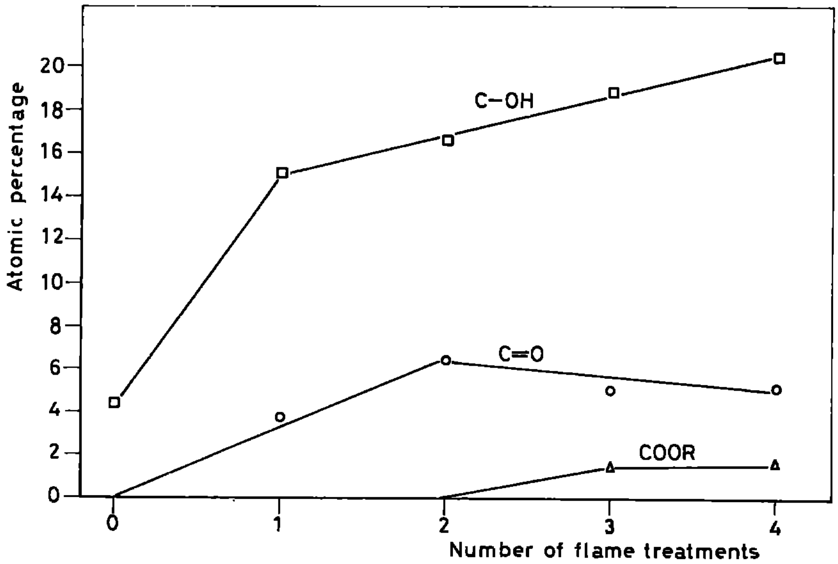

Figure 3 Plot of the atomic percentages of the various Cls components against the number of flame treatments (at 15 m min^{-1} and 4 cm from the burner).

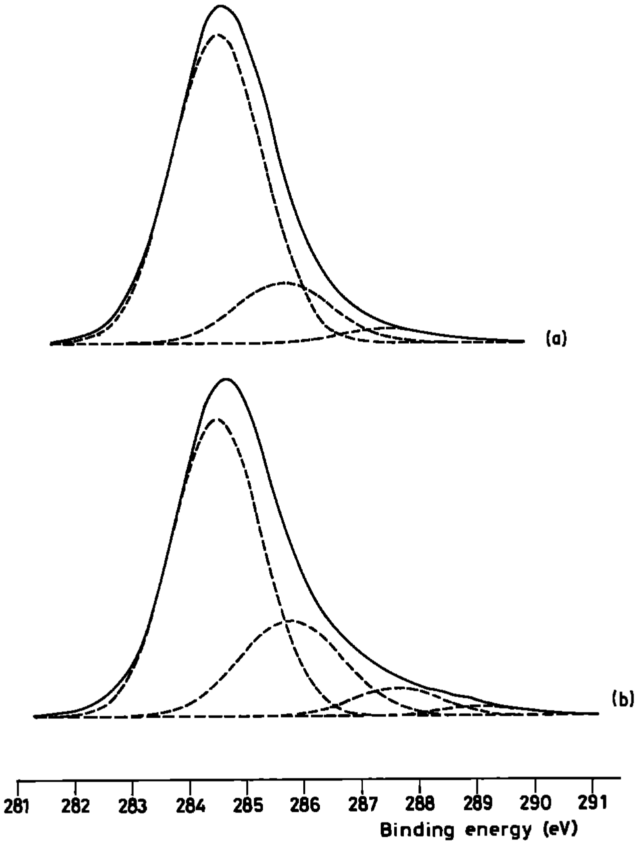

Figure 4 XPS O1s spectra of flame treated polypropylene: (a) one treatment, (b) four treatments.

bonds mainly). Both the surface tension and the polarity are functions of the modifications induced in the material by the treatment but perhaps also of the amount of contaminant present on the surface. In Fig. 5 polarity is shown as a function of flame treatments. The polarity increased with the first two treatments and decreased with the third and the fourth. The polarity of the samples treated once but more "harshly" is intermediate between those corresponding to one and two "normal" treatments, an analogous trend was observed for the chemical composition. The surface tension (Table III) shows a somewhat different behaviour. In particular it tends to decrease only with the fourth treatment.

TABLE IV Results of adhesion force test of paints on polypropylene samples

Sample	Adhesion force (kg)	
	Polyacrylic-polyester paint	Polyurethane paint
Untreated	< 5	< 5
1 Tr. (15 m min^{-1}, 4 cm)	160	150
2 Tr. (15 m min^{-1}, 4 cm)	160	150
3 Tr. (15 m min^{-1}, 4 cm)	170	150
4 Tr. (15 m min^{-1}, 4 cm)	170	160
1 Tr. (15 m min^{-1}, 2 cm)	160	150
1 Tr. (5 m min^{-1}, 4 cm)	170	160

It is interesting to observe how the relationship of polarity to flame treatments is related to the amount of the C=O component. In fact, a remarkable proportionality is noted in plotting the polarity against the atomic percentage of the C=O component for each sample (Fig. 6). Furthermore, the polarity of the surface decreases along with the appearance of carboxyl groups. In our opinion this effect of the presence of carboxyl groups is related to their tendency to form hydrogen bonds with other groups (for instance hydroxyl functions) within the surface. This would result in an inhibition of these groups to interact with the wetting solvent. The tendency to form hydrogen bonds is obviously less important in carbonyl groups, this could account for the slightly increased wettability in samples were there are no carboxyl groups.

Another possible explanation could be the formation of an important amount of low molecular weight chains as a consequence of repeated flame treatments. This phenomenon could partially account for the examined decrease in polarity and surface tension.

2.5. Adhesion to paint coatings

The debonding force of the paint coating over a given area, determined as shown in Fig. 1, is related to the bonding strength at the polymer/coating interface. The experimental results obtained for flamed polypropylene in comparison to the untreated sample are listed in Table IV. It is evident that the flame treatment

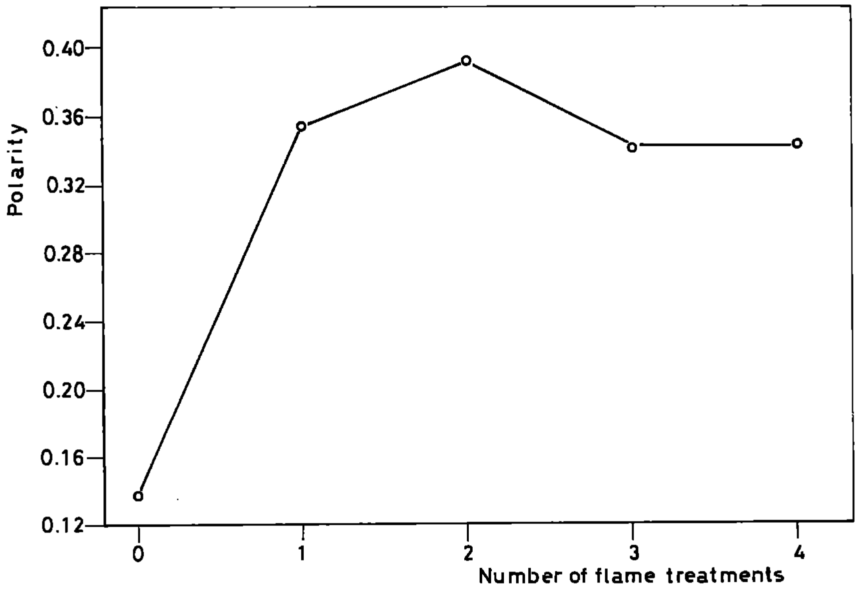

Figure 5 Plot of the polarity of the surface of flame treated polypropylenes against the number of flame treatments (at 15 m min^{-1} and 4 cm from the burner).

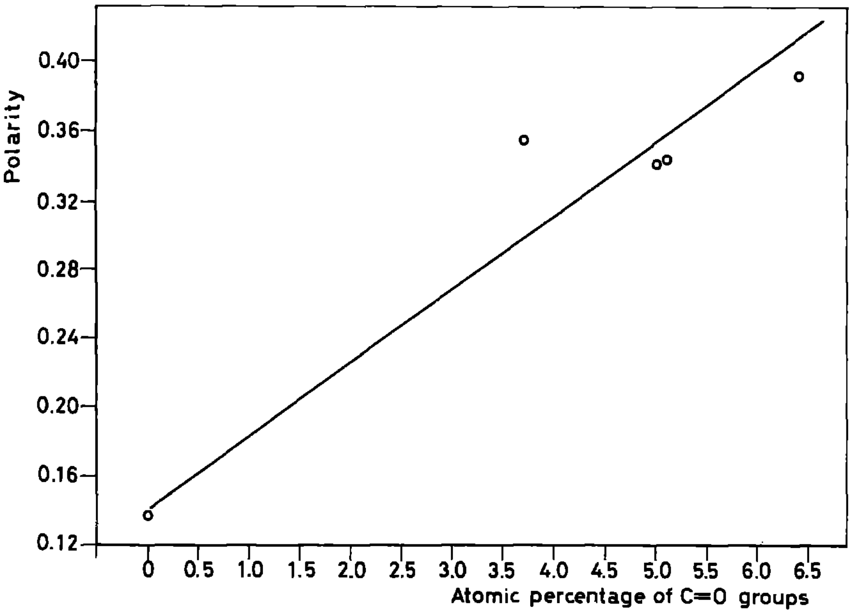

Figure 6 Plot of the polarity of the surface against the atomic percentage of the carbonyl function.

increases considerably the adhesion of the polymer to the coating. There is at least a factor of thirty in favour of the treated samples. Furthermore a single treatment appears sufficient to obtain strong adhesion. Further treatments do not significantly increase the strength of adhesion.

This phenomenon can be explained if the adhesion force is due mainly to polar groups present in the first one or two monolayers. The effect of further treatments would be to increase the depth of oxidation without affecting the effectiveness of adhesion.

3. Discussion

The surface oxidation of polypropylene has been obtained in the past few years using various treatments, but the mechanism has unanimously been considered by radicalic means [1–10]. In addition it is known that the chemical reactions evolving in a flame usually proceed through free radical intermediates [14]. So there is no reason to propose another mechanism for the introduction of oxygen containing functions through a flame treatment.

The first step of the proposed mechanism involves the formation of hydroperoxide species, reacting with time to form a number of different products (hydroxyl, carbonyl, carboxyl, ether, peroxide, etc., functions).

R–H ⟶ Radicalic intermediates

⟶ Products
(–C=O, –C–OH,
–COOR, –C–O–C–,
etc.)

The chemical composition presumed from our XPS data is quite consistent with this scheme.

The observation of a limited amount of oxygen containing functions even in the untreated sample is consistent with the findings of Carlson and Wiles [1–6].

The formation of carboxyl functions is particularly evident with the iteration of flame treatments. This would suggest ulterior oxidation of already existing functions (C–OH or C=O) as a major source of carboxyl groups. This would explain the decrease in the amount of carbonyl groups with the third and fourth flame treatments.

In a study of the printability of electric (corona) discharge treated polypropylene, Briggs and coworkers [8, 14] attributed the adhesion phenomena to the interaction of enolic groups on the surface with the coating. It has also been reported [14] that adhesion and wettability often respond differently to chemical treatments of the surface. Similar results have been observed in our case. The adhesion of the polymer to the paint coating remains quite constant after one treatment, while the composition in the first 3 to 5 nm shows some variations.

The variation in the quantity of polar groups observed through XPS can be attributed to an increase in the depth of oxidation with the number of treatments. At the same time there is also a qualitative variation (appearance of carboxyl groups). Evidently the polarity of the surface (physical entity) is more sensitive to the presence of carboxyl groups than the adhesion (a chemical phenomenon). The discrepancy can be attributed to the different forces acting in the two cases. In the first, only polar and dispersive interactions are important. In the second, chemical bonds are probably formed.

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