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The Formation of Crosslinked Polymer from Polyethylene in Benzenesulfonic Acid Aqueous Solution

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Polymer degradation was investigated by examining reactions with alternate daylight exposure and immersion in aqueous environments. Crosslinked polymers were produced by the carbonium ion reaction of carbonyl groups in benzenesulfonic acid aqueous solution.

Recently, the recovery of useful substances from the catalytic decomposition of waste plastics and polymer degradation by acid rain have been a matters attracting much attention in consideration of environmental pollution.[1—5] The reactions involved cannot be analyzed by ordinary polymer radical chain reactions, but rather by the reactions of polymer carbonium ions.

However, the reactivity of polymer carbonium ions participating in polymer degradation is virtually unknown while that of primary, secondary, and tertiary carbonium ions formed in the main chains of polymers has been studied to some degree.[6—8] Particularly in reactions in benzenesulfonic acid aqueous solution, the relationships between daylight exposure and immersion in benzenesulfonic acid aqueous solution and degradation by polymer carbonium ions are very little understood.[9,10]

The cationic degradation of polyolefin in acidic aqueous solution should differ markedly from that of radical degradation.

The reactions have usually been studied by analyzing SO_2 and CO_2 gas formation and measuring the induction periods of oxidation.[9] In this study, the behaviors of polymer carbonium ions or radicals participating in polyethylene degradation and formed in an aqueous environment and polymer reactions were examined by FT-IR observation of the changes in polymer surfaces.[8,11,12]

Experimental

Sample. The sample used was LDPE film (low density polyethylene, thickness=0.3 mm, density=0.910—0.925, $[\eta]=1.11$), cut to 0.03×1.5×5.0 cm.

Benzenesulfonic Acid Aqueous Solution and Aqueous Solution for Immersion. Benzenesulfonic acid (96% and above) was used for the preparation of benzenesulfonic acid aqueous solutions (hereinafter refered to as acidic solution) of various normalities. Normality was determined by sodium hydroxide aqueous solution (Factor=1.006) and the acidic solution was compared only with the aqueous solution (ion changed water hereinafter refered to as purified water).

Preparation. The reactor vessel for immersion was made from a Pyrex glass tube (inner diameter 2 cm, length 9 cm) and was placed in a hot water bath at a fixed temperature (60±2°C). The sample film was introduced into the reactor vessel containing 900 ml of acidic solution at each normality or purified water only.

In the case of immersion only, the reaction was performed by heating the hot water in which the polyethylene sample layers were immersed for 10 to 200 d. The reaction was usually carried out with exposure to daylight and immersion in each solution at 10-d intervals. The sample films were exposed to sunlight from the south and this induced degradation. The indoor and outdoor temperatures were then measured.

Analysis Method. Analysis of functional groups formed on the main chains of the polymer were carried out by absorptiometry using an FT-IR spectrometer (Perkin–Elmer 1600 type). The functional groups detected by absorption were carbonyl (>C=O), vinyl (C=C–), vinylidene (C=C(C)–), and vinylene (–C=C–) groups.[13,14] Absorbance was expressed as a ratio of the absorbance of each group to that of the methyl groups.

Results and Discussion

Reaction in Benzenesulfonic Acid Aqueous Solution and Aqueous Solution. In the oxidative degradation of polyethylene (hereinafter refered to as PE), oxidized volatile products, such as olefins, alcohols, and aldehydes are usually produced.[15,16]

–OH, –CHO, and –COOH groups on the main chains are also formed and oxidation of PE main chains take place. The formation of vinylene groups indicates abstraction of on-chain hydrogen atoms by hydroperoxide due to oxidative degradation. These unsaturated chains contribute to crosslinking and degradation of the polymer. Thus, the production of olefins and carbonyl groups must be studied for clarification of the degradation process.

By changing the ratio of the absorbance of other functional groups to the methyl groups in the main chain for before and after reaction in purified water, the viscosity (η) of oxidized PE was determined.

The initial absorbances of the functional groups in the sample without pretreatment were compared with those following the reactions. An increase in the absorbance

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of the functional groups after being immersed in the purified water was measured and the results are given in Table 1.

PE sample layers were immersed for oxidation in purified water in the reactor vessel fixed at 60°C. Changes in the functional group absorbances were observed by FT-IR. A 0 value in purified water indicated the initial absorbance of each layer.

As shown in Table 1, the carbonyl group absorption formed during 180 d immersion was 0.95 and was 20 times higher than the initial value. Similarly, those of the vinyl (C=C–) and vinylidene (C=C(C)–) groups were about 2—3 times the initial values. A peculiar phenomenon showing a marked disappearance of the C=C(C)– group absorbance was noted at 60 d or more of immersion. The absorption of the C=C(C)– group could not be detected after 60 d. The disappearance of the C=C(C)– group corresponded to an increase in the concentration of the carbonyl group. Consequently, crosslinked PE insoluble in hot xylene that could not be measured by viscometry was produced. This vinylidene disappearance and increase in the carbonyl group concentration were closely related to crosslinked polymer formation. Thus, hydroperoxide formed by the oxidation of unsaturated chains takes place to further scission the main chains and thereafter, crosslinking reactions by addition of unsaturated chain-ends may occur.

The results for each 20 d period when immersion and exposure were alternated every 10 d are given in Table 2. The reaction was similar to that of immersion in purified water as shown in Table 1. The oxidation of PE in purified water occurs easily, and thus should occur even more readily in this system. However, the concentrations of C=C– groups during the first 100 d formed in this alternation system was less than that in purified water. Similarly, that of C=C(C)– groups was 0.16 for the alternation system and 0.15 for purified water. For the carbonyl groups, the values were 0.49 for the present system and 0.63 for purified water only. Oxidation thus occurs to a greater extent in the water-immersion system. This was particularly evident with an increase in the number of days of immersion, e. g. the concentration of C=C(C)– groups formed by immersion for 160 d was 0.32, but was only 0.22 for the alternation system. The C=C– and C=C(C)– groups in the purified water system also disappeared, though in the alternation system there was no disappearance. The carbonyl concentration in this system increased rapidly after 100 d, thus showing that oxidative degradation proceeded vigorously in both systems. The reactions took place preferentially in the purified water for the same number of days of immersion. Of course, the viscosities of the polymer from both systems were impossible to determine. Different temperatures during daylight exposure (average 30 °C) and immersion (60 °C) may be the reason for this. Since diffusion of antioxidants into the water from the PE surface takes place, the oxidative degradation of the unstabilized PE surface should occur more easily, consequently, crosslinking reactions take place to a greater extent in the alternation system at higher temperatures.

Reactions at Different Normalities in the Benzenesulfonic Acid Aqueous Solution System. Table 3 shows the results for the oxidative degradation of PE immersed in different normalities in the acidic solution system. The most characteristic feature was that no carbonyl groups could be detected at any normality. As shown in Table 1, the concentration of each functional group increased with the number of days of immersion in purified water only, though no change in the initial values was noted for the acidic solution.

It came to a conclusion that no oxidative degradation occurs in this system. That is, no change in olefinic product concentration could be detected and this was not related to the disappearance of olefin signals and/or the increase in carbonyl group signals. The formation of olefinic product through abstraction of on-chain hydrogen atoms by a hydroperoxide is not important.

But an increase in molecular weight was observed in the acidic solution. Usually, the oxidative degradation of a polymer in an aqueous environment occurs by oxygen dissolved in water. Oxidation appeared in most cases to occur by oxygen dissolved in acidic solution as was the case of immersion in water.

Nevertheless, crosslinking reactions without oxidation occurred with the PE layers immersed in the acidic solution. Table 4 shows viscosity values of degraded PE layers during immersion in water and 3 equiv acidic solution. This value increased with the number of days of immersion and could not be measured for long periods of immersion.

This shows crosslinking reactions took place without oxidation in the PE layers. Viscosity could not be measured except in the layers obtained in early stage reactions. Of course, matter insoluble in hot xylene solvent was produced in the latter half of the reactions. The disappearance of carbonyl groups was also observed with an increase in the number of days of immersion and corresponded to the progress of the crosslinking reactions. That is, hydroperoxide did not participate in crosslinking reactions. It is evident that the reaction proceeds by polymer carbonium ions formed in this system.

When crosslinking reactions occur with unsaturated bonds in the main chains, insoluble PE must be formed in response to an increase in viscosity and the disappearance of the olefins. No change in olefin signals, however, was observed. The olefin groups were unrelated to the crosslinking reactions which may occur by other processes whose mechanisms have yet to be determined.

On the other hand, protonation of the unsaturated chain ends present at high concentrations occurs easily follow Scheme 1; the addition of olefinic chain ends to chain end carbonium ions takes place. Consequently,

Table 1. Changes in the Concentrations of the Functional Groups after Being Immersed in Purified Water

Functional groups	Methyl	Vinylidene	Vinyl	Vinylene	Carbonyl
Days					
0	1	0.073	0.082	0.059	0.051
10	1	0.060	0.067	0.049	0.042
20	1	0.060	0.060	0.043	0.036
40	1	0.072	0.080	—	—
60	1	0.073	0.081	0.066	0.154
80	1	—	0.108	0.096	0.330
100	1	—	0.160	0.158	0.627
120	1	—	0.214	0.225	0.989
140	1	—	—	0.262	1.053
160	1	—	—	0.316	0.934
180	1	—	—	—	0.955
200	1	—	—	—	0.815

Table 2. Changes in the Concentrations of the Functional Groups When Immersion (Purified Water) and Exposure Were Alternated Every 10 Days

Functional groups	Methyl	Vinylidene	Vinyl	Vinylene	Carbonyl
Days					
0	1	0.073	0.082	0.059	0.051
20	1	0.076	0.085	0.063	0.054
40	1	0.083	0.093	0.073	0.093
60	1	—	0.100	0.084	0.206
80	1	—	0.123	0.111	0.279
100	1	—	0.154	0.149	0.484
120	1	—	0.185	0.190	0.715
140	1	—	0.217	0.225	0.780
160	1	—	0.213	0.223	0.886
180	1	—	0.227	0.244	0.913
200	1	—	0.257	0.279	0.984

a soluble high molecular weight polymer produced by extension of the chain length should be produced with the disappearance of th olefinic signals.

No soluble high molecular weight polymer is produced. Crosslinking reactions may occur with internal olefins formed by carbonium ion reactions in the acidic solution.

The formation of internal olefins take place mainly as follow (Scheme 2) :9) The crosslinking reactions are unrelated to the initial unsaturated chains in the PE layers.

As shown in Scheme 2, they occur between on-chain carbonium ions and unsaturated bonds of the main chains. The migration of initial olefinic groups in the solid PE layers takes place with considerable difficulty. Consequently, these groups do not become involved in crosslinking reactions. The reactions take place between carbonium ions formed on the sample surface and newly unsaturated bonds formed with an increase in the number of days of immersion with the disappearance of carbonyl groups. Carbonyl groups are produced mainly on the polymer surface, thus, this disappearance may cause the formation of carbonium ions produced by protonation with carbonyl groups as shown in Scheme 3.

Reaction with Alternate Daylight Exposure and Immersion in Benzenesulfonic Acid Aqueous Solution. Table 5 shows the results of alternate 10 d intervals of daylight exposure and immersion in acidic solution. Comparing Table 5 with Table 2, the concentration of carbonyl groups by oxidation in this system can be seen to be 1/4 (60 d) or 1/6 (100 d) of that of the purified water-daylight exposure system. Oxidation was shown to be restrained by immersion in the acidic solutions. As shown in Table 3, no carbonyl group signals were detected during immersion in the acidic solution without daylight exposure. The restraint of oxidation in this system was similar to the results of immersion in the acidic solution.

The absorbance of the carbonyl groups increased by about 9.4 (100 d) and 18 (180 d) times the initial values for the purified water-daylight exposure system. The results of immersion were about 1.6 (100 d) and 3.0 (180 d) times the initial values for the acidic system. The increase in the ratio of the carbonyl group concentration was remarkably high for the former system. The acidic solution markedly affects the restraint of PE oxidative degradation. The presence of cations in the acidic solution may cause a change in the chemical structure of the PE surface and decomposition of the hydroperoxides. The PE layer surface may take on a stable structure to

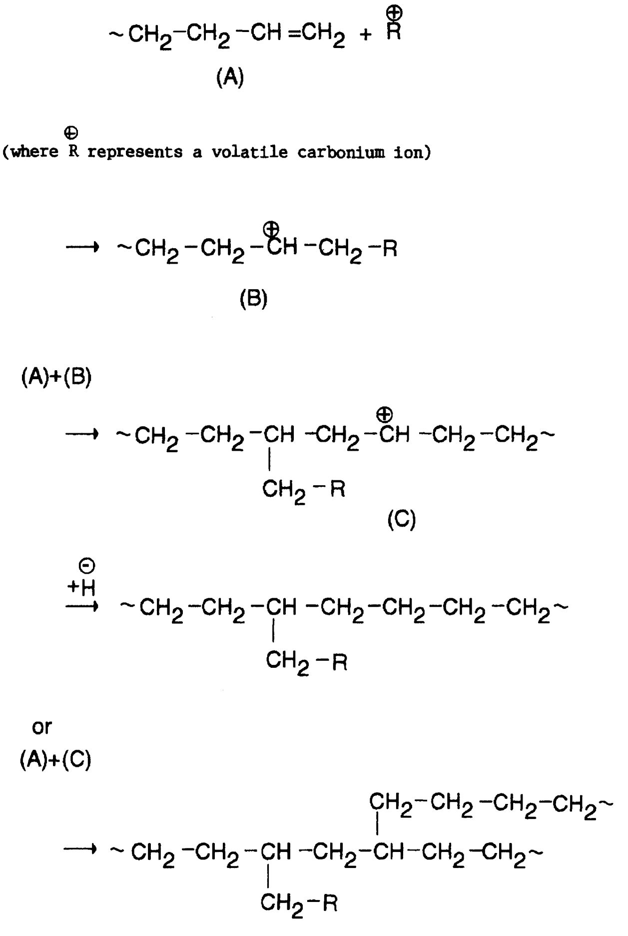
Table 3. Changes in the Concentrations of the Functional Groups after Being Immersed in Benzenesulfonic Acid Aqueous Solutions of Different Normalities

Functional groups		Methyl	Vinylidene	Vinyl	Vinylene	Carbonyl
Days	Normality					
0	1	1	0.073	0.082	0.059	0.051
	3	1	0.073	0.082	0.059	0.051
	5	1	0.073	0.082	0.059	0.051
	7	1	0.073	0.082	0.059	0.051
10	1	1	0.077	0.086	0.063	0.055
	3	1	0.076	0.084	0.062	0.053
	5	1	0.073	0.082	0.059	0.051
	7	1	0.066	0.074	0.053	0.043
20	1	1	0.063	0.071	0.051	0.042
	3	1	0.066	0.074	0.053	0.044
	5	1	0.072	0.080	0.058	0.048
	7	1	0.071	0.079	0.057	0.047
40	1	1	0.077	0.085	0.062	—
	3	1	0.065	0.072	0.053	—
	5	1	0.080	0.089	—	—
	7	1	0.076	0.084	0.062	—
60	1	1	0.074	0.082	0.060	0.154
	3	1	0.074	0.082	—	—
	5	1	0.077	0.085	0.063	—
	7	1	0.068	0.075	—	—
80	1	1	0.075	0.083	—	—
	3	1	0.072	0.080	—	—
	5	1	0.072	0.080	—	—
	7	1	0.064	0.071	—	—
100	1	1	0.069	0.077	—	—
	3	1	0.074	0.082	—	—
	5	1	0.074	0.081	0.059	—
	7	1	0.071	0.079	0.057	—
120	1	1	—	0.075	0.083	—
	3	1	0.072	0.080	0.058	—
	5	1	0.074	0.081	0.060	—
	7	1	0.076	0.083	0.061	
140	1	1	0.074	0.081	—	—
	3	1	0.073	0.081	—	—
	5	1	0.079	0.087	0.064	—
	7	1	0.071	0.079	0.058	—
160	1	1	0.072	0.080	0.058	—
	3	1	0.066	0.073	0.054	—
	5	1	0.077	0.085	0.063	—
	7	1	0.072	0.079	—	0.041
180	1	1	0.071	0.079	0.057	—
	3	1	0.073	0.081	0.059	—
	5	1	0.076	0.084	0.061	—
	7	1	0.072	0.080	0.059	—
200	1	1	0.053	0.061	—	—
	3	1	0.051	0.059	0.037	—
	5	1	0.054	0.063	0.039	—
	7	1	0.051	0.059	0.037	—

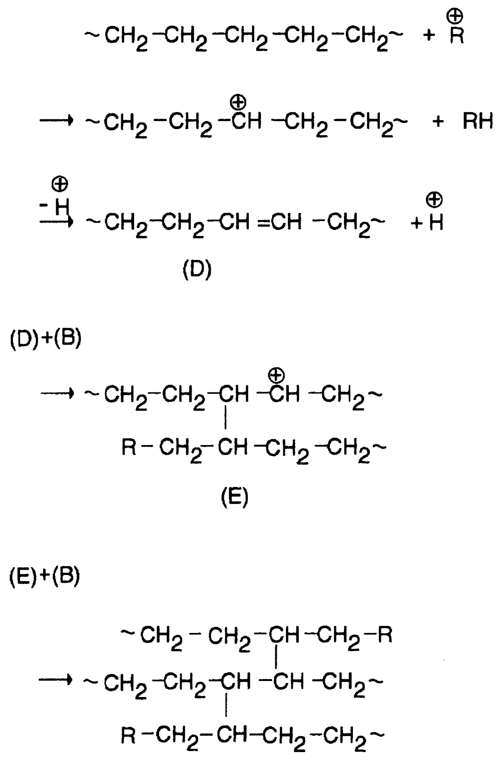
withstand oxidation during daylight exposure.

On the other hand, as shown in Fig. 1, the concentration of the carbonyl groups gives an indication of the rapid increase from the initial value of the functional groups for the purified water-daylight exposure system and the slight increase from the initial value for the acidic solution-daylight exposure system. The rate of oxidation in the latter system is remarkably slow. In the case of immersion in acidic solution only, the cross-linking reactions occurred without oxidation, with the disappearance of carbonyl groups with an increase in the number of days of immersion.

From these experimental results, the carbonyl group concentrations shown in Table 5 may represent a decrease in the amounts of carbonyl group concentrations which disappeared by protonation with carobonyl



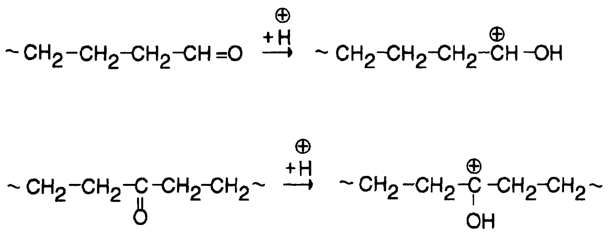
Scheme 1.



Scheme 2.

Table 4. Viscosity Values of Degraded Polyethylene Layers during Immersion in Purified Water and 3 equiv Benzenesulfonic Acid Aqueous Solution

Sample		Viscosity $[\eta]$
Starting PE		1.12
Purified water	Immersion 10 d	1.20
3 equiv Benzenesulfonic acid aqueous solution	Immersion 20 d	1.38
3 equiv Benzenesulfonic acid aqueous solution	Immersion 40 d	1.61



Scheme 3.

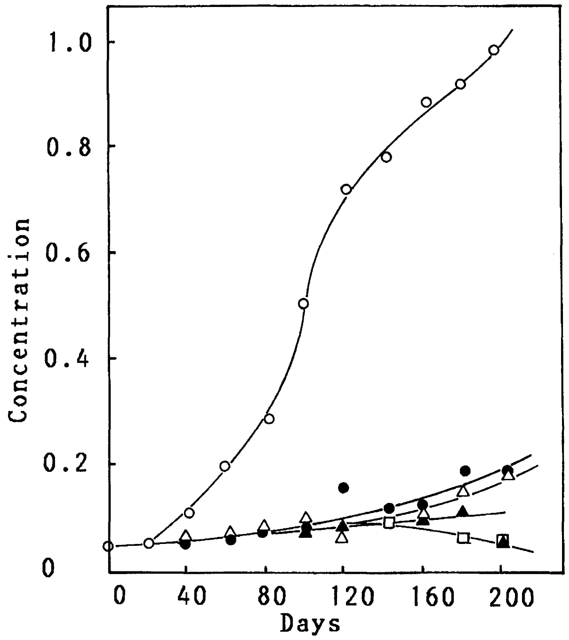


Fig. 1. The changes in the concentrations of the carbonyl groups for purified water and benzenesulfonic acid aqueous solution immersion-daylight exposures. ○; purified water, ●; 1 equiv, △; 3 equiv, ▲; 5 equiv, □; 7 equiv.

groups participating in the formation of crosslinked polymers as shown in Scheme 2. It is evident from Table 3 that carbonyl groups participated in the crosslinking reactions in the acidic solution.

Vinylidene groups participate in the crosslinking reaction in the purified water system, but not in the crosslinking reactions in the acidic solution. In the case of the purified water system, allylic hydrogen atoms in the vinylidene olefin undergo hydroperoxide oxidation easily through radical chain reactions, however, these

Table 5. Changes in the Concentrations of the Functional Groups When Immersion (Benzenesulfonic Acid Aqueous Solution) and Exposure Were Alternated Every 10 Days

Functional groups		Methyl	Vinylidene	Vinyl	Vinylene	Carbonyl
Days	Normality					
0	1	1	0.073	0.082	0.059	0.051
	3	1	0.073	0.082	0.059	0.051
	5	1	0.073	0.082	0.059	0.051
	7	1	0.073	0.082	0.059	0.051
20	1	1	0.074	0.082	0.061	0.054
	3	1	0.068	0.077	0.056	0.048
	5	1	0.071	0.079	0.058	0.050
	7	1	0.066	0.075	0.054	0.046
40	1	1	0.069	0.076	0.058	0.048
	3	1	0.079	0.087	—	0.057
	5	1	0.076	0.084	0.063	0.053
	7	1	0.077	0.085	0.064	0.053
60	1	1	0.072	0.081	0.061	0.054
	3	1	0.073	0.082	0.063	0.060
	5	1	0.074	0.083	0.063	0.052
	7	1	0.080	0.090	0.069	0.054
80	1	1	0.070	0.079	0.061	0.067
	3	1	0.079	0.080	0.071	0.073
	5	1	0.080	0.090	0.070	0.054
	7	1	0.078	0.087	0.068	0.060
100	1	1	0.080	0.091	0.072	0.079
	3	1	0.070	0.081	0.064	0.092
	5	1	0.069	0.078	0.061	0.071
	7	1	0.075	0.084	0.066	0.074
120	1	1	—	0.104	0.087	0.155
	3	1	—	0.093	0.075	0.050
	5	1	—	0.091	0.073	0.074
	7	1	0.072	0.082	0.065	0.083
140	1	1	—	0.109	0.093	0.100
	3	1	—	0.094	0.076	0.106
	5	1	—	0.102	0.083	0.110
	7	1	0.076	0.089	0.070	0.093
160	1	1	—	0.092	0.078	0.157
	3	1	—	0.101	0.085	0.145
	5	1	—	0.100	0.083	0.133
	7	1	—	0.086	0.069	0.117
180	1	1	—	0.109	0.094	0.196
	3	1	—	0.099	0.085	0.151
	5	1	—	0.096	0.080	0.113
	7	1	0.067	0.078	0.061	0.088
200	1	1	—	0.095	0.082	0.196
	3	1	—	0.089	0.076	0.194
	5	1	—	0.060	0.044	0.067
	7	1	—	0.075	0.054	0.081

functional groups produce tertiary and secondary carbonium ions in the acidic solution. Specifically, tertiary carbonium ions from vinylidene olefin represent a lower reactivity than that of other groups, therefore, no crosslinking reactions occur at stable tertiary carbonium ions. The mechanisms of the crosslinking reactions in the acidic solution have yet to be determined. These crosslinking reactions may occur by way of Schemes 2 and 3. In this system, it became clear that crosslinked polymers are produced through the reaction of carbonyl groups in the acidic solution.

Conclusion

Polymer degradation was studied by examining reactions with alternate daylight exposure and immersion in aqueous environments. The results were as follows: PE layers undergo ordinary oxidation by reaction with daylight exposure and immersion in purified water. Oxidation was found to be restrained by immersion in benzenesulfonic acid aqueous solution.

Vinylidene groups participate in the crosslinking reaction in the purified water system, but not in the crosslinking reactions in the acidic solution. In the acidic solution system, crosslinked polymers are produced through the carbonium ion reaction of carbonyl groups produced during immersion in the acidic solution.

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