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Effect of pH Coagulation and Sulphuric Acid as a Coagulant on Natural Rubber Properties

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This paper re-examines the use of sulphuric acid as a coagulant for natural rubber latex. It also discusses the effect of pH of coagulation and treatment of coagulum on the raw rubber properties, rheometric cure properties of ACS-1, ISO and tread mixes, and physical properties of vulcanisates of ISO and tread mixes. Heat ageing and stress decay of these vulcanisates are also examined. Sulphuric acid as a coagulant does not severely alter the raw rubber properties if the pH of coagulation is kept at pH 5. The resultant rubbers have lower Mooney viscosity, and are marginally inferior in tensile properties on heat ageing. Rubbers coagulated with sulphuric acid at pH below 3.5 have distinctly poorer ageing properties.

Processing natural rubber latex using sulphuric acid as a coagulant is discouraged[1,2] because the rubber thus prepared behaves differently from its formic acid counterpart. Excessive use of sulphuric acid[3] affects the durability of the raw rubbers adversely and any residue of the non-volatile acid present in the dry rubber may be harmful and influence the cure characteristics. On the contrary, some researchers[4,5] claimed that use of the right proportion of sulphuric acid does not affect the intrinsic properties of the raw rubber, and the amount of free residual sulphuric acid present in the dry rubber is not significantly large enough to alarm manufacturers. It was also observed[6] that rubber coagulated by excessive sulphuric acid tended to have retardation in cure, especially in an unaccelerated rubber/sulphur mix, but the accelerated compounds were not affected.

This paper re-examines the effect of sulphuric acid as a coagulant on rubber properties, particularly, the ageing behaviour both in raw and vulcanised states. Oven ageing and stress relaxation were used to assess the thermal ageing characteristics of these rubbers.

EXPERIMENTAL

Bulk latex from the RRIM Experiment Station was ammoniated at 0.05% to ensure its stability during collection and transportation. The dry rubber content (d.r.c.) was determined, and 0.04% (based on d.r.c.) of sodium metabisulphite and 0.1% castor oil were added. The resultant latex was divided into eight equal portions and classified for two series of experiments. One series was coagulated at pH 5.0, and the other series at pH 3.5. Within each series, four samples were coagulated using a mixture of formic acid and sulphuric acid in the ratios 1:0, 2:1, 1:2 and 0:1 weight/weight. The coagula were then left overnight.

Each coagulum was divided into two portions. One portion was creped with continuous flow of water, washing away the excess coagulant. This type of rubber was classified as 'with washing'. The other portion of coagulum was creped without any water flowing, *i.e.* 'without washing'. Latex was also coagulated at other pH values such as pH 3.0 and pH 2.0. The dry rubbers prepared were tested for the normal SMR properties. Technological eva-

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luations using ACS-1 and ISO were carried out in accordance with ISO/BSI test procedures[7,8]. A tread mix was also evaluated.

Stress Relaxation

The rubber compounds chosen for stress relaxation were:

	Mix A	Mix B
Rubber	100	100
ZnO	5	5
Stearic acid	2	2
CBS	0.6	0.6
Sulphur	2.55	2.55
Flectol H	–	1.0

One of them had an antioxidant effective in the oxidative resistance against molecular oxygen. The rubber vulcanisate was stretched at 70% strain, allowed to relax physically overnight and stress relaxation was measured at 94°C. The stress was continuously monitored until it was reduced to about 50% of its original value. The reduced stress is given as f/fo where f is the stress at time t, and fo the stress at 1 minute.

RESULTS AND DISCUSSION

Raw Rubber Properties

Effect of pH. The Plasticity Retention Index (PRI) is a fairly good measure of the susceptibility of natural rubber to thermal oxidation[9]. The effects of the pH of coagulation and of type of acids (or mixture) on PRI are shown in *Figure 1.* At pH of above 3.5, the type of acid used does not significantly influence the value of PRI. However, at pH values below 3.5, the ratio of the mixture of the two acids influences the PRI values; the PRI decreases with increase of sulphuric acid in the coagulant mixture. In fact, it was observed that the dry rubbers prepared by coagulation of latex at pH 3.0 and below were more tacky, visually more 'oxidised' and had very low PRI. This study compares raw and vulcanised rubber properties of rubber samples prepared from coagulation at pH 5 and pH 3.5, and wherever possible rubbers coagulated below pH 3.5 or at pH 2.0 have been included.

Generally, low pH of coagulation gave low values of plasticity (P_0), Mooney viscosity (V_R), higher nitrogen content and darker colour *(Table 1).* When sulphuric acid was used instead of formic acid, the values of P_0 and V_R were reduced further in both CV (constant viscosity) rubber and non-viscosity stabilised rubber *(Table 2).* The PRI was marginally affected. The other SMR properties were similar. Sulphuric acid coagulated rubbers were darker and had slightly higher ash content[10].

Effect of washing. The purpose of washing was to examine the influence of the residues of the coagulant. At pH 5, the properties were not affected by the residues (with no washing) of acid in the rubber since washing did not improve the properties significantly *(Table 3).* The sulphuric acid coagulated rubber, however, had a small amount of residual sulphates. Rubber coagulated at low pH without washing had a higher level of sulphates and high metallic ion content *(Table 4).* Some of these metallic ions probably have pro-oxidant properties[11,12], and can be responsible for auto-catalytic oxidation[13,14], thus lowering the PRI value during ageing. However, this was not vividly observed in the course of the experiments. Washing reduced both the metallic ion and sulphate levels and did not affect the PRI significantly[15].

Cure Behaviour in ACS-1 Mix

A comparison of the vulcanisate properties of different rubbers is not simple, and is more complex than a comparison

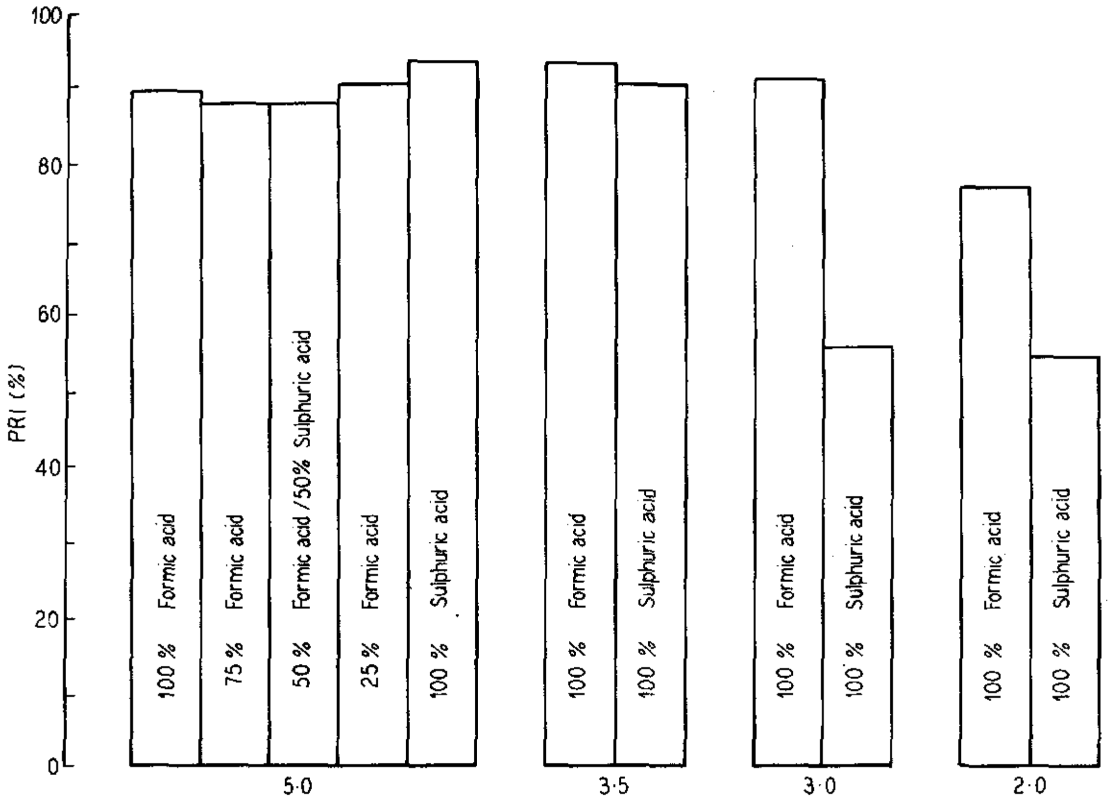

Figure 1. Plasticity retention index of rubbers coagulated at pH 2.0 to pH 5.0.

TABLE 1. EFFECT OF pH ON RAW RUBBER PROPERTIES

Property	Formic acid pH 5.0	Formic acid pH 3.5	Formic acid pH 2.0	Sulphuric acid pH 5.0	Sulphuric acid pH 3.5	Sulphuric acid pH 2.0
V_R	73	65	63	69	61	59
P_0	48	43	41	45	39	36
PRI (%)	86	89	77	89	85	54
N_2 (%)	0.41	0.40	0.48	0.40	0.41	0.49
Ash (%)	0.25	0.22	0.23	0.27	0.26	0.27
Colour (lovibond units)	3.0	4.0	5	3.0	5.0	9

of the raw rubber properties because for vulcanised rubbers, a constant basis for comparison, such as fixed curative level or hardness, must be selected. The alternative method of comparing only optimised properties is frequently not experimentally possible. The problem is less complicated in the comparison of the rubbers under consideration as the rubbers are similar in chemical structure, but even here the different responses to curative discussed above must be taken into account.

TABLE 2. EFFECT OF pH ON VISCOSITY OF RUBBERS

Rubber	Formic acid pH 5.0	Formic acid pH 3.5	Sulphuric acid pH 5.0	Sulphuric acid pH 3.5
Non-viscosity stabilised	74	63	68	59
Viscosity stabilised	68	58	55	53

TABLE 3. EFFECT OF WASHING TREATMENT ON RAW RUBBER PROPERTIES AT pH 5.0

Property	Formic acid With washing	Formic acid No washing	Sulphuric acid With washing	Sulphuric acid No washing
V_R (mean) range	68	69	65	65
P_0 (mean) range	44	45	42	41
PRI (%)	88	87	88	90
N_2 (%)	0.40	0.40	0.40	0.41
Ash (%)	0.22	0.24	0.28	0.27
Colour (lovibond units)	3.0	4.0	4.0	4.0

TABLE 4. PRO-OXIDANT METALLIC ION AND SULPHATE CONTENTS IN RAW RUBBERS

Item	Formic acid				Sulphuric acid			
	pH 5.0		pH 3.5		pH 5.0		pH 3.5	
	Washing	Without washing	Washing	Without washing	Washing	Without washing	Washing	Without washing
Pro-oxidant metallic ion (p.p.m.)	5.7	4.8	3.7	6.0	6.1	13.5	7.2	13.7
Iron content (p.p.m.)	6.9	4.2	8.4	4.8	4.2	12.7	4.6	12.2
Total heavy[a] metallic ion content (p.p.m.)	6.7	5.7	6.3	6.9	8.0	14.5	8.5	14.6
Residual sulphate SO_4^{-2} (% wt)	–	–	–	–	0.16	0.26	0.20	0.37

[a]Iron, copper and manganese

Apart from the raw rubber properties, the other important parameter is the cure behaviour of the rubber. The rheometric trace was used to characterise the cure behaviour but Mooney scorch was also measured. Irrespective of the coagulant, a low pH of coagulation (pH 3.5 and below) gave a more scorchy and faster curing rubber; but its modulus or degree of vulcanisation remained at a similar level *(Table 5)*. Use of sulphuric acid instead of formic acid did not affect the cure behaviour, in fact, the final rubber was observed to be marginally less scorchy, especially at pH 5.0. It was observed that washing did not affect the cure behaviour *(Table 6)*.

Cure and Ageing Properties in ISO Mix

The ISO mix was designed primarily to test synthetic polyisoprene (IR) and it resembled a typical factory formulation. *Table 7* shows the technological properties of rubbers coagulated at pH 5 and pH 3.5. Using either acid as coagulant, a lower pH results in shorter scorch time, shorter optimum cure time and faster cure rate. The modulus indicated by change in rheometric torque (ΔT) remained unaffected. The influence of low pH of coagulation was more marked in the ISO mix than in the ACS-1 mix. The physical properties of the rubber vulcanisates irrespective of pH values of coagulation and

TABLE 5. EFFECT OF pH OF COAGULATION ON THE BEHAVIOUR OF RUBBERS IN ACS-1 MIX

Property	Formic acid		Sulphuric acid	
	pH 5.0	pH 3.5	pH 5.0	pH 3.5
Scorch time, t_2 (min)	5.2	4.6	5.6	4.7
Optimum cure time, t_{90} (min)	34.1	36.0	35.4	33.0
Cure rate, $t_{90} - t_2$ (min)	30.8	28.3	20.8	28.4
Torque, ΔT (N-m)	1.42	1.37	1.35	1.44
Mooney scorch T_5 at 120°C (min)	6.0	5.8	7.8	6.2

TABLE 6. EFFECT OF WASHING ON THE CURE BEHAVIOUR OF RUBBERS IN ACS-1 MIX

Property	Formic acid		Sulphuric acid	
	Washing	No washing	Washing	No washing
Cure behaviour at 140°C				
Scorch time, t_2 (min)	4.5	4.8	5.2	5.1
Optimum cure time, t_{90} (min)	35.3	34.8	34.6	33.8
Cure rate, $t_{90} - t_2$ (min)	30.8	28.8	29.4	28.7
Torque, ΔT (N-m)	1.40	1.39	1.40	1.40
Mooney scorch, T_5 at 120°C (min)	6.1	5.7	7.0	6.9

TABLE 7. EFFECT OF pH ON THE TECHNOLOGICAL PROPERTIES OF RUBBERS IN ISO MIX

Property	Formic acid		Sulphuric acid	
	pH 5	pH 3.5	pH 5	pH 3.5
Cure behaviour at 140°C				
Scorch time, t_2 (min)	6.3	4.5	6.8	4.3
Optimum cure time, t_{90} (min)	21.0	18.3	21.5	18.7
Cure rate, $t_{90} - t_{20}$ (min)	14.7	13.8	14.7	14.4
Torque, ΔT (N-m)	3.51	3.55	3.47	3.38
Mooney scorch, T_5 at 120°C (min)	19.6	13.2	22.2	12.6
Physical properties of vulcanisate cured at 40 min/140°C				
Tensile strength (MN/m^2)	29.2	28.7	30.0	29.1
Elongation at break (%)	510	510	530	550
M300 (MN/m^2)	14.0	12.8	12.4	11.4
MR100 (MN/m^2)	1.98	2.02	2.02	1.89
Hardness (IRHD)	60.0	61.0	62.0	62.0
Dunlop resilience (%)	79.1	78.4	79.9	76.8
Aged properties 1 day/100°C				
Tensile strength (MN/m^2)	9.1	8.3	10.2	8.8
Retention (%)	30	29	34.2	30
Elongation at break (%)	220	280	300	290
Retention (%)	43	55	57	53
M300 (MN/m^2)	9.1	–	10.2	–
Retention (%)	65	–	82	–
Change in hardness	+ 1.0	+ ½	+ ½	0

Rubber 100, Zinc oxide 5; stearic acid 2; sulphur 2.25; Santocure NS 0.7; IRB3 35. Cured at 140°C/40 min

type of acid, were observed to be almost identical. The aged properties were also similar and their differences were observed to be within experimental error.

Cure and Ageing Properties in Tread Mix

The evaluation of a typical tread mix with 50 p.h.r. HAF black was also included in this study, the results are shown in *Table 8*. The influence of pH of coagulation on the cure behaviour was marked. Low pH value gave a more scorchy and faster curing compound, the effect of the type of acid was not predominant. At pH 5.0, the cure behaviour was not affected by the type of acid, though sulphuric acid gave a slightly slower rate of cure and less scorchy rubber.

The aged tensile properties of rubbers coagulated by sulphuric acid were observed to be poorer. Irrespective of pH value, sulphuric acid coagulated rubbers were 10% – 15% lower in retention of tensile strength and elongation at break than formic acid coagulated rubbers. Other physical properties were identical.

TABLE 8. EFFECT OF pH OF COAGULATION ON THE TECHNOLOGICAL PROPERTIES OF RUBBER IN A TREAD MIX

Property	Formic acid		Sulphuric acid	
	pH 5.0	pH 3.5	pH 5.0	pH 3.5
Cure behaviour at 140°C				
Scorch time, t_2 (min)	6.8	4.6	7.0	4.5
Optimum cure time, t_{90} (min)	29.0	23.0	32.0	25.7
Cure rate, $t_{90} - t_2$ (min)	22.2	18.4	25.4	21.2
Torque, ΔT (N-m)	3.47	3.46	3.16	3.29
Mooney scorch T_5 at 120°C (min)	18.5	12.8	21.0	13.0
Physical properties of vulcanisates cured at 40min/140°C				
Tensile strength (MN/m^2)	27.1	26.1	27.1	25.1
Elongation at break (%)	540	520	550	500
M100 (MN/m^2)	2.5	2.4	2.5	2.6
M300 (MN/m^2)	11.9	11.8	11.8	12.6
Hardness (IRHD)	65.5	65.5	63	66.5
Dunlop resilience (%)	62.8	65.2	65.3	65.6
Aged properties 1 day/100°C				
Tensile strength (MN/m^2)	14.4	15.0	9.2	11.3
Retention (%)	53	57	34	44
Elongation at break (%)	360	380	300	300
Retention (%)	67	73	55	60
M300 (MN/m^2)	11.5	10.8	9.2	11.3
Retention (%)	97	92	78	—

Effect of Metal Salts on Ageing

The rubbers prepared by coagulation using sulphuric acid were contaminated by high iron content[15]. Traces of metallic ions [12, 13] especially in the form of metal salts of long chain fatty acids, had been shown to be a significant factor influencing the oxidative degradation of raw and vulcanised rubbers. The data presented so far indicated that low pH of coagulation and the use of sulphuric acid affected adversely the ageing properties of the rubber and its vulcanisate, *i.e.* low PRI and aged tensile values. A further evaluation of ageing was made and substantiated by using stress relaxation, and to determine whether the type of acid and pH of coagulation influenced the ageing properties.

Figure 2 shows the spectra of stress relaxation of unprotected and protected vulcanised rubbers. In spite of their differences in initial stress relaxation rates it can be seen that all the curves were of similar shape; the stress relaxation rate increased steadily from the start and eventually reached a low value. It is apparent that the iron content present in the rubber influenced the rate of stress relaxation[16,17]. However, the rubber containing 26 p.p.m. of iron had slightly lower levels of stress decay in its final stage, even though its initial rate was observed to be higher than those of rubbers containing 17 p.p.m. of iron.

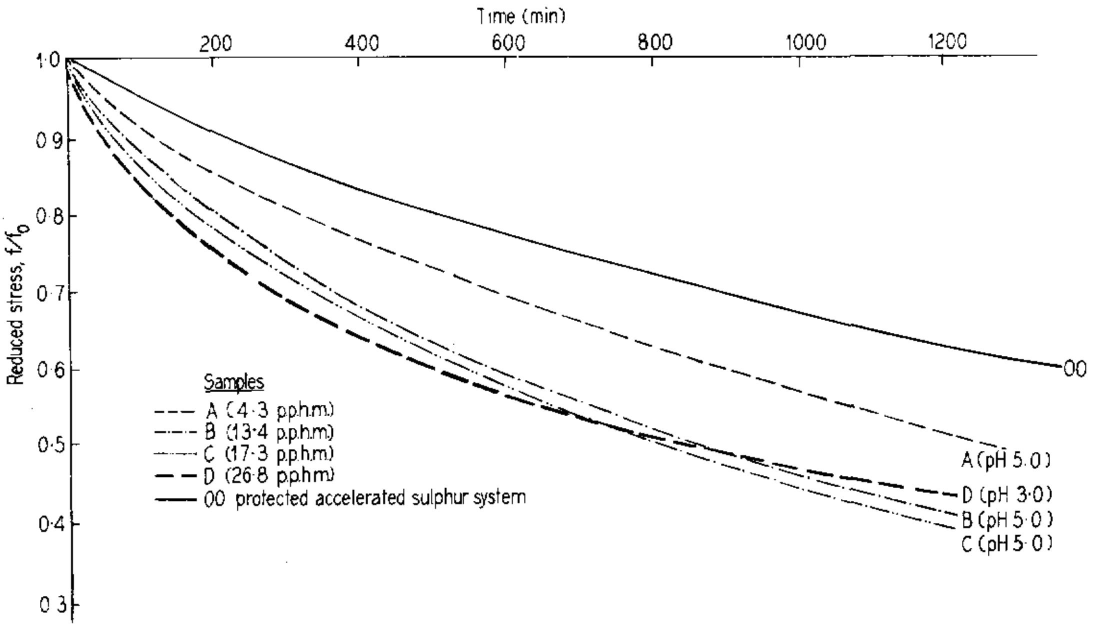

Figure 2. Effect of iron content on stress relaxation of an unprotected accelerated sulphur system measured at 94° C.

By plotting the logarithms of stress decay against time in the initial stage, a straight-line relationship was obtained *(Figure 3)*. The slopes of the straight lines are measures of stress relaxation rates. It is observed that this increases with increasing iron content. It is reasonable to presume from this observation that iron acts as a pro-oxidant in vulcanised natural rubber, accelerating basic oxidation.

When these rubbers were compounded using Flectol H as an antioxidant, the sttress relaxation spectra were shifted upwards and coincided with the spectrum (00) in *Figure 2*. It is possible to reduce the stress relaxation by protecting the vulcanisate using Flectol H. Thus, vulcanised natural rubber containing excessive metallic ion content such as iron can be protected against oxidation using antioxidant e.g. Flectol H. This observation has also been confirmed by other workers[12, 13].

CONCLUSION

The pH of coagulation has a pronounced effect on viscosity. Lowering the pH of coagulation from 5 to 3.5 reduces the viscosity of raw rubber by 7 to 10 Mooney units. A further drop of 4 units is observed if sulphuric acid replaces formic acid as the coagulant. The reduction is evident in both CV and non-viscosity stabilised rubbers. Generally, other raw rubber properties are similar, except that rubbers coagulated by sulphuric acid tend to have 15% higher ash content. Washing during processing does not affect the general raw rubber properties except that

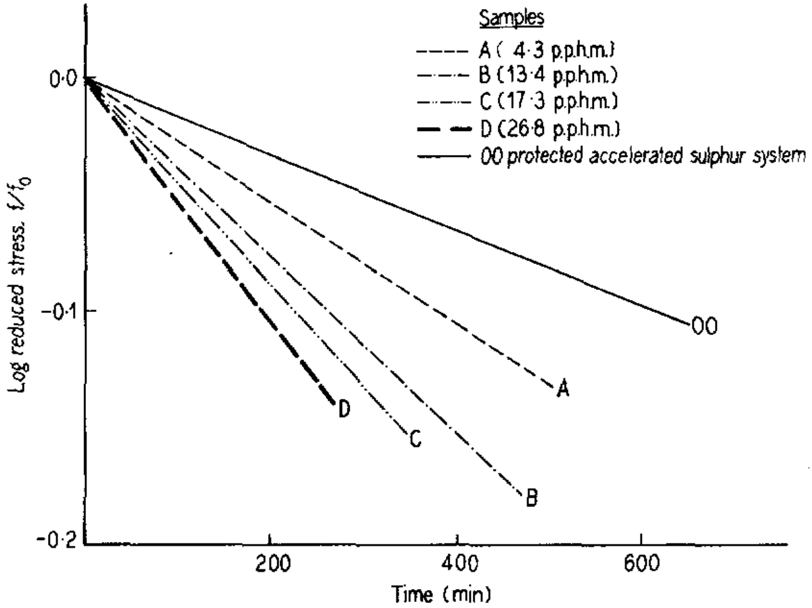

Figure 3. Effect of iron content on the rate of stress relaxation at 94°C.

the metallic ion contamination is reduced. The PRI is affected only when the pH drops below 3.5, particularly when sulphuric acid is used.

In the ACS-1 mix, the pH of coagulation tends to have a more pronounced effect on the cure behaviour than the type of acid. A low pH produces a slightly more scorchy and faster curing rubber. The effect of pH of coagulation is surprisingly more marked in the ISO and tread mixes. A low pH of coagulation generally gives rise to a scorchy and faster curing rubber.

The ageing behaviour of sulphuric acid coagulated rubbers as measured by aged tensile properties are distinctly inferior in the tread mix. The effect is less evident in the ISO mix. This poorer ageing properties of sulphuric acid coagulated rubbers are confirmed by stress relaxation studies. These studies also indicated the adverse influence of low pH of coagulation.

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