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Ammonium Perchlorate, Friend or Foe?

Part II: The Specific Interaction Between Ammonium Perchlorate, Nitroglycerine and Polyethylene Glycol

Ruth Tunnell,*[a] Mark Ashcroft,[a] Roz Dale,[a] Dave Tod,[a] and William G. Proud[b]

Abstract: In part 1 of this paper, it was demonstrated that a nitroglycerine and polyethylene glycol based propellant containing ammonium perchlorate degraded at a slower rate at temperatures of 80 °C or less compared with the other two energetic materials studied which did not have this oxidizer present. It was suggested that ammonium perchlorate might act as an oxygen inhibitor reducing the oxidation rate of the polyethylene glycol binder which decreases the rate of propellant decomposition. In part 2, the specific inter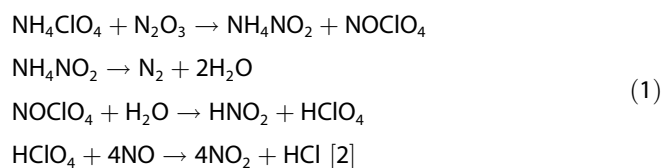action between ammonium perchlorate, nitro-glycerine and polyethylene glycol is reported. It has been shown that at temperatures lower than 90 °C, if there is any uncured and unstabilised PEG present, nitroglycerine rapidly degrades in the presence of ammonium perchlorate but this is prevented if stabiliser is added. In addition, ammonium perchlorate initially appears to hinder acid hydrolysis of nitroglycerine which also slows down the degradation of polyethylene glycol based propellants. However, in the long term at low temperatures, or short term at higher temperatures, AP accelerates the decomposition of NG.

Keywords: Ammonium perchlorate · Nitroglycerine · Polyethylene glycol · Propellant · Aging

1 Introduction

At elevated temperatures, or at lower temperatures such as 80 °C over long time periods, a propellant composition, containing polyethylene glycol (PEG), AP and nitroglycerine (NG), suddenly and violently ignites without prior warning such as a gradual temperature rise or the evolution of brown fumes [1].

This behavior has been attributed to the fact that at high temperatures, in the presence of NG, AP can degrade to form perchloric acid. This causes the rapid hydrolysis of the nitrate ester and can also directly react with the oxides of nitrogen evolved as NG undergoes degradation (Equation (1)) [2–4].

$$NH_4ClO_4 + N_2O_3 \rightarrow NH_4NO_2 + NOClO_4$$

$$NH_4NO_2 \rightarrow N_2 + 2H_2O$$

$$NOClO_4 + H_2O \rightarrow HNO_2 + HClO_4 \tag{1}$$

$$HClO_4 + 4NO \rightarrow 4NO_2 + HCl \; [2]$$

Previously, researchers have reported that compositions incorporating NG and AP have lower shelf lives than analogous materials which do not contain this oxidizer [5–8]. However, these conclusions were drawn from heating experiments at elevated temperatures such as 130.5 °C [5].

In part 1 of this paper it was demonstrated that a propellant composition containing AP along with NG and PEG degraded at a slower rate than the other two materials studied which did not incorporate this oxidizer [1]. The reasons for these observations have been further investigated using a range of analytical techniques.

2 Experimental Section

2.1 Aging of NG

All of the aging experiments involving NG were carried out in 3 cm³ glass vials, hermetically sealed with a Teflon lined lid. The samples were placed for up to 16 days in a block bath at 80 (±0.1) °C before analysis.

For the samples that were analyzed by High Performance Liquid Chromatography (HPLC), initially triacetin (TA) was added to the NG and NG/AP mixtures to act as a desensitizing agent. To yield 100 mg samples, equal parts by mass of the components were used. Once it had been proved that there was no need to include TA, the total sample mass was increased to 200 mg. The NG was also aged in the presence of 2-nitrodiphenylamine (2-NDPA) and paranitro-

[a] R. Tunnell, M. Ashcroft, R. Dale, D. Tod
QinetiQ Fort Halstead
Sevenoaks, Kent, TN14 7BP, UK
Fax: +1959-516041
*e-mail: rtunnell@qinetiq.com

[b] W. G. Proud
Institute of Shock Physics
Imperial College
London, SW7 2AZ, UK

methylaniline (pNMA). The following mixtures were aged and then subjected to HPLC:

1. NG in isolation.
2. NG/AP.
3. NG/PEG.
4. NG/PEG/AP.
5. NG with 1% 2-NDPA and 1% pNMA.
6. NG/AP with 1% 2-NDPA and 1% pNMA.
7. NG/PEG with 1% 2-NDPA and 1% pNMA.
8. NG/PEG/AP with 1% 2-NDPA and 1% pNMA.
9. NG with 1% 2-NDPA, 1% pNMA and 0.7% water.
10. NG/AP with 1% 2-NDPA and 1% pNMA and 0.7% water.
11. NG/PEG with 1% 2-NDPA, 1% pNMA and 0.7% water.
12. NG/PEG/AP with 1% 2-NDPA and 1% pNMA and 0.7% water.

Samples were also aged, in the same manner, for ion chromatography (IC) and NMR spectroscopic analysis. It was found that TA interfered with the results from these techniques so dibutyl phthalate (DBP) was used as the desensitizing agent instead. This appeared to have no effect on the analysis of the samples. The single exception was for the sample aged at 90 °C in the presence of AP, which completely decomposed, analysis showed that the DBP had degraded.

The total sample mass used was 200 mg and equal components by mass were subjected to aging. The mixtures therefore either contained NG and DBP or NG, DBP and AP. The samples were aged for five days in a block bath at 70, 80, or 90 °C. The temperature was controlled to within ±0.1 °C.

2.2 Analytical Methods

It should be noted that in all cases, duplicate samples were used. The data are given as an average and the results are reported as being significant if the differences in the values are greater than the standard deviation for the set of data analyzed.

Acidity analysis was carried out using a similar method to that of McDonald [9]. The NG/triacetin (TA) sample mass was 0.25 (±0.05) g NG and 0.20 (±0.05) g TA where as for the NG/TA/AP experiments, all of the compounds weighed 0.16 (±0.04) g. The samples for acidity analysis were heated in 3 cm^3 glass vials, hermetically sealed with a Teflon lined lid. The samples were placed for 5 in a block bath at 80 (±0.1) °C or 90 (±0.1) °C before analysis.

HPLC was performed with a Dionex HPLC Ultimate 3000 instrument. The column used was a Lichrosorb RP_18 (5 μm) fitted with a Lichrospher 100 RP_18 (5 μm) guard.

For IC, analysis was performed using a Dionex DX500 machine fitted with suppressed conductivity detection. The columns used were an AS4A and AS11.

NMR spectroscopic analysis was performed using a Bruker Avance 400 spectrometer, proton frequency 400 MHz, fitted with a 5 mm QNP probe. The samples were extracted in a deuterated solvent and quantification was achieved through the addition of tetrakis(trimethyl)silane (TTMS) which acted as an internal standard.

3 Results and Discussion

The results from the first set of aging experiments involving NG and AP mixed with TA are shown in Table 1. Initially, there was greater NG degradation when AP was present but after longer periods of time, 14–16 days, comparison shows the reverse.

The results were considered surprising. It was not expected that such levels of NG would be recovered at longer times from mixtures containing AP. The experiments were repeated, this time no desensitizing agent was used, but the effect of adding PEG to the mixture was investigated. The results are given in Table 2.

The NG and NG/AP samples were withdrawn after just five and six days as the lids of the sample vessels had popped open. It was not known why they produced gas, indicating the severe decomposition of the nitrate ester, after a relatively short aging time. There was insufficient residue in the vials for the value of NG to be reliable.

Comparing the NG and NG/AP experiments, after seven days, it can be seen that there was significantly more NG remaining when AP was in the mixture. However, when PEG was introduced, there was rapid decomposition of NG when AP was present. Probably the AP readily oxidizes the

Table 1. Amount of NG recovered from samples aged at 80 °C with triacetin.

Aging condition	Sample	% NG recovered
7 days	NG/TA	94.48
14 days	NG/TA	1.74
16 days	NG/TA	1.02
7 days	NG/TA/AP	75.48
14 days	NG/TA/AP	41.64
16 days	NG/TA/AP	43.71

Table 2. Amount of NG recovered from further samples aged at 80 °C without triacetin.

Aging condition	Sample	% NG recovered
5 days	NG	5.70
7 days	NG	0.51
6 days	NG/AP	None
7 days	NG/AP	85.86
7 days	NG/PEG	68.43
14 days	NG/PEG	73.01
7 days	NG/AP/PEG	0.53
14 days	NG/AP/PEG	0.85
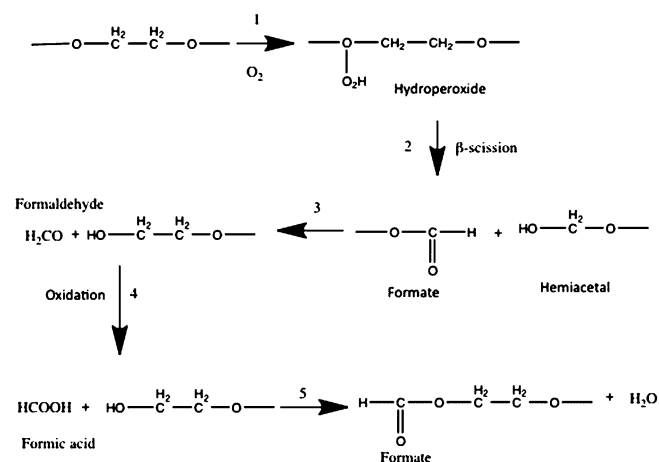
Scheme 1. Reproduced from Ref. [10].

uncured PEG leading to the production of compounds such as formic acid, lowering the pH and catalyzing the degradation of NG (Scheme 1) [10].

The results also suggest that PEG has a stabilizing effect on NG as a relatively high amount of the nitrate ester was recovered after aging. This might be because oxygen reacts with PEG in preference to the NG and so slows the decomposition of the nitrate ester. Further research is required to understand the exact mechanisms behind this data.

NG and NG with AP were then aged in the presence of 2-NDPA and pNMA, both with and without tap water, which was also added to the samples. The results are in Table 3.

Table 3 shows once again, after aging for seven days at 80 °C, there was more NG and overall lower stabilizer degradation when AP was absent. However, by 14 days, not only was there a comparatively greater concentration of NG left when AP was present but there was significantly less stabilizer depletion.

The opposite appears to occur when water is present though. After seven days, there was slightly more NG recovered and a greater amount of total stabilizer remaining with AP. After 14 days, there was comparatively less NG in the AP containing mixture.

Closer inspection of the data shows that in general, there was less stabilizer depletion in the AP containing mix-

tures. These results suggest that the presence of AP affects the stabilizer degradation mechanisms. Usually, where both pNMA and 2-NDPA are present, the pNMA depletes preferentially, the 2-NDPA does not decompose until the concentration of pNMA has significantly decreased [11].

However, this degradation mechanism could be an artefact of analysis. Research performed at Waltham Abbey in the 1980's showed that in a mixture of pNMA and 2-NDPA, extracted in hot dichloromethane, the pNMA reacts with one of the 2-NDPA degradation products – N-nitroso-2-nitro-Diphenylamine (NNS-2NDPA) – to give N-nitroso-methyl-4-nitroaniline (NNSpNMA) and regenerate apparently unreacted 2-NDPA. The extent of this process depended upon temperature, time spent in the solvent and the presence of light [12].

This was confirmed by Bellerby *et al.* [13] who reported that reactions between pNMA and 2-NDPA can occur in extracts from propellants for HPLC analysis. It was suggested that NNSpNMA could react with the 2-NDPA to form an equilibrium with pNMA and NNS-2NDPA.

However, it is possible that AP interferes with the transnitrosation reaction; this prevents the pNMA reacting with 2-NDPA degradation products. Further research is required to understand the influence of AP on pNMA and 2-NDPA.

The effect of adding PEG to the mixtures was then assessed, the results are given in Table 4.

From Table 4 it appears that with AP, a greater amount of NG and stabilizer is recovered. This holds if water is added to the mixture. These results are in contrast to those in Table 2 and suggest that the stabilizers have a protective effect on PEG preventing oxidation.

The results of the acidity testing on mixtures of NG with and without AP are shown in Table 5. It was noted that when the NG/TA samples were removed from the block bath, there were brown fumes on the sides of the glass ampoule indicating that there were oxides of nitrogen present. However, for the samples containing AP there were no signs of brown fumes.

Table 5 illustrates that the NG was slightly acidic. It is possible that the pH of this mixture had fallen during storage due to the accumulation of nitric acid as NG decomposes, even at ambient temperature.

The data also reveals that while there was no significant difference in the pH level for the samples aged at 80 °C,

Table 3. HPLC results for samples aged with stabilizers and water.

Aging condition	Details	%NG recovered after aging	%2-NDPA recovered after aging	%pNMA recovered after aging
7 days	NG/stabilizers	88.47	89.18	57.98
14 days	NG/stabilizers	87.43	28.37	3.60
7 days	NG/AP/stabilizers	82.47	77.71	60.85
14 days	NG/AP/stabilizers	89.47	75.74	26.03
7 days	NG/stabilizers/water	88.60	84.25	57.47
14 days	NG/stabilizers/water	86.00	68.59	23.47
7 days	NG/AP/stabilizers/water	89.75	86.56	74.08
14 days	NG/AP/stabilizers/water	82.01	74.31	49.29

Table 4. HPLC results for samples aged with stabilizers and PEG.

Aging condition	Sample	%NG recovered after aging	%2-NDPA recovered after aging	pNMA recovered after aging
7 days	NG/PEG/stabilizers	87.24	82.96	50.74
14 days	NG/PEG/stabilizers	86.69	None	None
7 days	NG/AP/PEG/stabilizers	94.23	92.52	86.51
14 days	NG/AP/PEG/stabilizers	87.56	76.69	39.55
7 days	NG/PEG/stabilizers/water	89.51	85.93	38.22
14 days	NG/PEG/stabilizers/water	87.63	None	None
7 days	NG/AP/PEG/stabilizers/water	92.31	89.14	76.13
14 days	NG/AP/PEG/stabilizers/water	91.74	83.38	59.56

Table 5. pH testing results for samples aged with and without AP.

Aging condition	Sample	Change in pH relative to pH of distilled water
None	NG	−1.4
5 days 80 °C	NG/TA	−9.03
5 days 80 °C	NG/TA/AP	−9.05
5 days 90 °C	NG/TA	−9.63
5 days 90 °C	NG/TA/AP	−9.30

Table 6. Mass loss on aging.

Aging condition	%Mass loss samples without AP	%Mass loss samples with AP
5 days 70 °C	4.0	3.2
5 days 80 °C	4.0	3.0
5 days 90 °C	4.2	39.8

Table 7. Concentration of 1,2-DNG and 1,3-DNG after aging.

Aging condition	%1,2-DNG	%1,3-DNG
5 days 70 °C	0.09	0.06
5 days 70 °C with AP	0.17	0.07
5 days 80 °C	0.63	1.25
5 days 80 °C with AP	0.50	1.03
5 days 90 °C	2.69	2.73
5 days 90 °C with AP	0.00	0.00

the mixtures aged at 90 °C without AP were more acidic. This suggests that under these aging conditions, the AP initially neutralizes some of the nitric acid formed by NG decomposition.

Before any IC and NMR spectroscopic analysis was performed on the NG mixtures, the weight of the sample vial was recorded before and after aging. The results are given in Table 6.

At 70 and 80 °C, the mass loss from the vials containing AP was less than when AP was absent. This suggests lower degradation of NG as decomposition forms gaseous species and hence the sample loses mass. However, for the AP containing samples aged at 90 °C, it was found that the vial lid had been disturbed due to the production of gas. The mixture was a brown color indicating significant NG decomposition. Consequently, no degradation products such as 1,2-dinitroglycerine (1,2-DNG) and 1,3-dinitroglycerine (1,3-DNG) were detected using NMR in in this sample (Table 7) due to the gases lost.

In the sampling for the NMR spectroscopic analysis, slightly more NG was collected than was theoretically expected from the samples with AP. This suggests greater NG products were present than anticipated. This was a disadvantage of one sample being divided between different analytical techniques. In future the entire sample mixture will be extracted for a single analysis.

This may account for the fact that there was a slightly higher amount of 1,2-DNG present in the AP containing sample at 70 °C. At 80 °C, there is more when AP is absent. This agrees with the results in Table 5 and suggests that at this temperature, AP is hindering the hydrolysis of NG. However, at 90 °C, this was not the case as the sample with

AP completely degraded. So any AP stabilizing effect was not significant in this test.

The IC results are shown in Table 8.

If the results from the 90 °C samples are discounted, as only the residue from the AP containing specimen could be analyzed after the complete decomposition, then it is clear from Table 8 that when AP was present, there was significantly less nitrate and nitrite compared to the AP free sample. Again, AP could be initially hindering the accumulation of nitric acid. As a result, the overall decomposition of NG is slowed compared to when acidic compounds are able to increase in concentration. The exception to this is at the highest temperature (90 °C) where the AP appeared to accelerate the decomposition of NG.

The data from the NG mixtures to date are variable which complicates the interpretation. At 80 °C, one of the NG and the NG/AP mixtures rapidly decomposed. Yet, other samples, aged at the same time using the same NG, did not even after being heated for 16 days at 80 °C. At 90 °C, the sample for IC and NMR spectroscopic analysis containing NG and AP, completely degraded whereas the NG/TA/AP sample survived for five days. It is not known why the rapid decomposition occurred with some samples and not with others.

Table 8. IC results for samples aged with and without AP.

Aging condition	% Nitrate	% Nitrite
5 days 70 °C	0.0442	0.0553
5 days 70 °C with AP	0.0146	0.0382
5 days 80 °C	0.0468	0.8257
5 days 80 °C with AP	0.0247	0.0035
5 days 90 °C	0.1113	0.510
5 days 90 °C with AP	0.000	0.0857

The HPLC results were also variable. Sometimes AP proved beneficial for the NG whereas on other occasions there was less NG recovered from the mixture with AP. However, it is evident that AP does not routinely have a detrimental effect on NG and does not seem to accelerate decomposition under the aging conditions employed. The exception to this is when PEG is present without stabilizer and there is then rapid degradation of the NG. It is likely that AP oxidizes the PEG producing formic acid, lowering the pH and so the NG undergoes hydrolysis. Eventually, the AP degrades to form perchloric acid causing rapid decomposition as it reacts directly with the oxides of nitrogen (Equation (1)) and it can also cause rapid acid hydrolysis of this compound [3].

However, with PEG, stabilizers and AP in the mixture, there was more NG and stabilizers left after aging. It is possible that the presence of AP enhances the antioxidant properties of 2-NDPA as suggested previously [14].

The fact that the 90 °C samples were less acidic and there were no brown fumes in the AP containing mixture suggests that the AP may hinder the evolution of the oxides of nitrogen. This leads to the decrease in the amount of nitric acid produced.

The Russian chemist Lurie [2] studied the kinetics of the decomposition reactions when AP is mixed with the nitrate esters. He found that this oxidizer has different effects on the thermal decomposition of the nitrate ester depending on its structure. Lurie divided the nitrate esters into different classes depending on the position of the nitrate groups relative to each other. He showed that for nitrated alcohol esters where the nitro groups were divided by at least one carbon atom such as triethylene glycol dinitrate (TEGDN) and ethylene glycol trinitrate (EGTN), AP strongly accelerates the decomposition. This is evident by the fact that it decreases the time before autocatalysis occurs and causes positive acceleratory autocatalytic reactions, as measured by gas production.

For compounds such as nitrocellulose and dioxyethylnitramine dinitrate (DINA), AP moderately increased the rate of decomposition. However, Lurie did report that AP does not appear to affect the rate of thermal decomposition of NG. In addition, for compounds such as 1,6-hexandiol dinitrate (HDDN) there is no acceleration in the decomposition when AP is present which he stated was typical for nitrates with divided nitrate groups and with three and more carbon atoms associated with one nitrate group.

Lurie suggested that the reasons for the observations were that the oxides of nitrogen from the degradation of compounds such as EGTN can react with AP leading to the generation of perchloric acid (Equation (1)). This does not appear to occur when NG is mixed with AP, which suggests that AP inhibits the evolution of the oxides of nitrogen.

Furthermore, Eisele and Klöhn reported the compatibility of ammonium perchlorate with NG and trimethylolethane trinitrate (TMETN) as measured by the loss of mass from samples when heated at 105 °C for 8–72 hours. This showed that chemical stability is not impacted by the addition of AP to a mixture of NG and TMETN [15].

It is known that the thermal decomposition of NG between 80 and 140 °C occurs in two stages. The first of these is not influenced by the decomposition products. The second step is and this results in the rapid decomposition of the nitrate ester [16].

The activation energy for hydrolysis of NG to 1,2-DNG, 1,3-DNG and nitric acid is of the order of 71 kJ mol^{-1}. The thermal decomposition for nitrate esters requires about 150 kJ mol^{-1}. The rapid self-acceleration of nitrate ester degradation occurs due to the oxidative and hydrolytic interaction of NG with nitric acid, nitrogen dioxide and water. If any of these are present there will be acid hydrolysis of the ether bond in the NG followed by oxidation of the resultant DNG. At lower temperatures, nitric acid increases the decomposition, while water is more important at higher temperatures. This probably explains why water was not a significant influence on the rate of NG degradation in these experiments. Additionally, anything that binds or eliminates nitric acid, water or oxides of nitrogen will prevent the acceleration of the NG decomposition. These processes are illustrated by Equation (2) [3]:

$$3NO_2 + H_2O \rightarrow 2HNO_3 + NO \tag{2}$$

The results imply that in the main, AP initially slows down the decomposition of NG by hindering the hydrolysis of NG to 1,2-DNG and 1,3-DNG and by possibly reacting with the nitric acid formed to yield compounds such as ammonium nitrate. The acid hydrolysis process may also be slower when AP is present because compounds can adsorb onto the surface of this oxidizer. However, further experiments are required to elucidate the exact mechanisms for this.

As a result, less nitrate and nitrite are produced when AP is present and it also seems likely that the nitrate formed is at least partly due to ammonium nitrate and not entirely nitric acid. Unfortunately, it is not possible distinguish these two compounds using IC analysis and initial attempts using NMR spectroscopy were unsuccessful.

At elevated temperatures or long times at lower temperatures, such as 80 °C, though, the decomposition of NG is able to reach a significant point in the presence of AP. This leads to the rapid degradation of the nitrate ester. This is because nitric acid and more importantly perchloric acid

reaches a critical concentration. The perchloric acid can cause rapid acid hydrolysis [3] or directly react with the oxides of nitrogen from NG (Equation (1)). Ultimately hydrochloric acid forms and the result is rapid propellant degradation and ignition.

4 Conclusions

It has been shown that AP has a significant influence on the aging behavior of both NG and PEG.

Uncured PEG in mixtures with NG and AP is rapidly oxidized by AP leading to the fast decomposition of NG. However, if stabilizer is present this has a protective effect on both the PEG and NG. The results suggest that PEG might help decrease the rate of NG degradation but further experiments are needed to clarify this.

At low temperatures in the short term (less than 90 °C) AP appeared to slow the acid hydrolysis of NG. This may be because it possibly reacts with any nitric acid that forms. In addition, lower concentration of nitrite containing species are detected suggesting that when AP is present, any nitrous acid is more likely to be neutralized, possibly via the reaction with oxygen to form nitric acid, and then nitric acid may react with ammonium perchlorate. Again, further experiments are needed to elucidate the exact mechanisms occurring.

However, if AP containing propellants are heated at high temperatures (greater than 90 °C), or for long periods at lower temperatures such as at 80 °C, then perchloric acid accumulates and can no longer be neutralized. This either causes rapid acid hydrolysis of NG or there is direct reaction between the oxides of nitrogen and the products from the decomposition of NG. This leads to the rapid degradation of propellants containing NG, PEG and AP and ultimately, the propellant suddenly ignites.

Therefore, overall, AP can be a friend or foe depending on the conditions imposed.

Symbols and Abbreviations

DBP	dibutyl phthalate
DINA	dioxyethylnitramine dinitrate
DNG	dinitroglycerine
1,2-DNG	1,2-dinitroglycerine
1,3-DNG	1,3-dinitroglycerine
EGTN	ethylene glycol trinitrate
HDDN	1,6-hexandiol dinitriate
HTPB	hydroxy terminated polybutadiene
IC	ion chromatography
HPLC	high performance liquid chromatography
NC	nitrocellulose
2-NDPA	2-nitrodiphenylamine
NG	nitroglycerine
NMR	nuclear magnetic resonance
pNMA	*N*-methyl-4-nitroaniline
TA	triacetin
TEGDN	triethylene glycol dinitrate
TTMS	tetrakis(trimethyl)silane

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