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Determination of Residual Extractable Hydroxylamine in Raw and Vulcanised Rubbers

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The accurate determination of hydroxylamine in rubber products is of particular importance when they are in contact with the human body or foodstuffs. In these applications, hydroxylamine must be below a specified limit. When the method developed for raw rubber is applied to vulcanisates, artificially high levels of hydroxylamine may be found due to the extraction of both zinc and calcium salts which react with 8-hydroxyquinoline to give a green colouration. The situation is further complicated in that, upon neutralisation of an extractant containing calcium or zinc salts, precipitates are formed which, when removed, appear to occlude some of the green colouration. This could artificially depress the apparent hydroxylamine concentration.

A method has been developed which enables the interference from zinc to be removed by the use of CDTA (trans-1,2-diaminocyclohexane-N,N,N′,N′-tetra acetic acid monohydrate), but interference from calcium has not yet been overcome.

Hydroxylamine salts are added to natural rubber (NR) latex before coagulation in order to react with low levels of carbonyl groups present in the rubber. The deactivated carbonyl groups are thereby prevented from undergoing reactions after coagulation which would result in the rubber hardening on storage[1]. This viscosity-stabilised rubber is designated CV (constant viscosity) rubber.

The original addition of hydroxylamine to the latex is made at a level of 0.15% weight/weight (equivalent to 1500 r.p.m.) based on the dry rubber content. After coagulation, washing and drying, the residual extractable hydroxylamine content falls to 50–200 p.p.m. depending upon the grade. This decreases further on compounding and even further on vulcanisation so that it is often undetectable in the finished product.

This point was appreciated by the West German Authorities, who do not permit hydroxylamine to be present in rubbers in contact with foodstuffs, and they agreed to the use of CV rubber provided that the hydroxylamine concentration *in the vulcanised product* was below 1 p.p.m. (based on the rubber) when a detailed and precisely described analytical procedure was carried out.

Hydroxylamine reacts with 8-hydroxyquinoline through an intra-molecular reduction which yields the amine 5-amino-8-hydroxyquinoline. This is then oxidised by atmospheric oxygen to the indo-oxine 5,8-quinolinequinone-5-(8-hydroxyquinolylimide) which imparts the green colouration to the alkaline test solution. An investigation into the applicability of this reaction for determining the hydroxylamine content of raw rubbers was carried out by Berg and Becker[2] and it seems probable that the translation to vulcanisates was carried out on the assumption that there would be no differences. It was, however, noted as early as 1968 by Higgins[3] that solutions obtained from vulcanisates were sometimes cloudy when their visible spectra were recorded and a filtration or centrifugation step was introduced to clarify them. It was also noted[3] that this precipitate was sometimes green in colour and, as the hydroxylamine-8-hydroxyquinoline adduct is also green, it was possible that this was being occluded by the precipitate, giving rise to a reduced value for the observed hydroxylamine content.

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The opposite effect was observed with zinc salts. These are solubilised by the acid extraction procedure and give a green colour with 8-hydroxyquinoline. This results in an enhanced value being obtained for the hydroxylamine content and, indeed, would appear to prelude any vulcanisate passing the German test.

More recent studies have shown that some other inorganic fillers capable of extraction with dilute acid — particularly calcium compounds — can give a green colour with 8-hydroxyquinoline. However, as most of the vulcanisates which can come into contact with foodstuffs are unfilled, or black filled, a method has been developed which gives a realistic assessment of the hydroxylamine content of these. If the inorganic components of the vulcanisate contain cations other than zinc any positive result must be considered suspect unless it has been shown that the particular cation does not interfere with the determination.

Methods for the determination of hydroxylamine in both raw and vulcanised natural rubber are reported in full.

EXPERIMENTAL

Determination of Hydroxylamine in Raw Rubber

Reagents. Analytical Reagent Grade was used wherever possible:

8-hydroxyquinoline solution — 1% weight/volume in ethanol (freshly made up)
$1M$ sodium carbonate solution
$0.8M$ sulphuric acid.

Method.

Extraction

Thinly sheeted raw rubber (5 g), cut into narrow strips, are immersed in 45 ml $0.8M$ sulphuric acid in a 150 ml round-bottom 24/29 neck flask and boiled under reflux for not less than 16 h.

The acid extract is decanted into a 50 ml volumetric flask and the rubber washed with $0.8M$ H_2SO_4. A second extraction of the rubber sample may yield additional hydroxylamine. This is determined separately as below and the two results added together.

Estimation

One millilitre of the $0.8M$ sulphuric acid extraction solution is placed in a 14/23 stoppered test tube (30 ml capacity) followed by 1 ml ethanolic 8-hydroxyquinoline solution and 3 ml of sodium carbonate solution. Oxygen is bubbled through this solution for 5 min; the tube is then stoppered and heated in a water bath at 40°C for 20 min. After cooling, the solution is transferred to a 10 ml volumetric flask and diluted to the mark with water. If a precipitate forms, the solution is filtered before filling a 1 cm spectrophotometre cell, and the absorbance is determined at 700 nm. The amount of hydroxylamine is found by reference to a calibration curve.

Calibration curve

Solutions containing 0, 4, 8, 12, 16, 20 μg per millilitre hydroxylamine in $0.8M$ sulphuric acid are made up by diluting a concentrated stock solution to the required strength. One millilitre of these diluted solutions is used and treated as described above.

Results

From the calibration curve of absorbance against concentration (microgramme per millilitre) of hydroxylamine the amount of hydroxylamine present in the extract can be found as H microgramme per millilitre.

$$\text{Hydroxylamine content of the rubber in parts per million} = \frac{H \times 50}{\text{Sample weight in gramme}}$$

(unless further dilutions have been made when the dilution factor should be included).

Determination of Hydroxylamine in Mixes and Vulcanisates

Reagents. Analytical Reagent Grade was used wherever possible:

8-hydroxyquinoline solution — 2% weight/volume in ethanol (freshly prepared)
1*M* sodium carbonate solution.

12.5*M* and 1*M* sodium hydroxide solution

CDTA (trans-1,2 diaminocyclohexane — N,N,N′,N′-tetra-acetic acid monohydrate) solution — 5 g CDTA is dissolved in 40 ml 1*M* sodium carbonate solution, and the solution filtered. The pH is adjusted to about 11 with 12.5*M* sodium hydroxide solution and then accurately to pH 11.2 using 1*M* sodium hydroxide solution. This solution is then diluted to 50 ml with 1*M* sodium carbonate solution.

Method.

Extraction

Raw mixes are thinly sheeted and cut into narrow strips, vulcanisates are crumbed on a mill. Test portions of 5 g each immersed in 45 ml 0.8*M* sulphuric acid in a 150 ml round-bottom 24/29 neck flask and boiled under reflux for not less than 16 h. The extract is then decanted into a 50 ml volumetric flask and the residual rubber washed with 0.8*M* sulphuric acid. The washings are then added to the extract in the volumetric flask and the contents diluted to 50 ml with 0.8*M* sulphuric acid. A second extraction of the rubber sample may yield additional hydroxylamine. This is determined separately as below, and the two results added together.

Estimation

One millilitre of the acid extract solution is placed in a 14/23 stoppered test tube (30 ml capacity). Three millilitres fresh CDTA solution is added and mixed thoroughly. One millilitre ethanolic 8-hydroxyquinoline solution is added and oxygen is bubbled through the solution for 5 min; the tube is then stoppered and heated in a water-bath at 40°C for 20 min. After cooling, the solution is transferred to a 10 ml volumetric flask and diluted to the mark with water. If a precipitate forms, the solution is filtered before determining the absorbance at 700 nm in a 1 cm spectrophotometre cell. The amount of hydroxylamine is found by reference to a calibration curve.

Calibration curve and results

These are as described above for raw rubber. (In the above procedure the slope of the calibration curve may vary with age of reagents and precise experimental conditions. The curve remains linear however. It is preferable therefore to obtain a calibration at the same time as the unknown solution is measured. If this is not possible, it is essential that *at least one* standard hydroxylamine solution be measured, the absorbance obtained, and ratioed against the absorbance measured for a hydroxylamine solution of the same strength, read from a previously determined valid calibration curve to obtain a 'correction factor'.)

DISCUSSION

Method Development

Some of the basic work detailing the modified method will be described before continuing to discuss the results obtained. Initial work using the acetic acid method showed that erratic results were obtained if levels of less than 8μg hydroxylamine were being determined. These erratic results were in part improved by close control of the pH of the extract solution, while much more reproducible results were obtained when 0.8*M* sulphuric acid was added to the acetic acid extract solution before the colouration stage. Using the acetic acid — sulphuric acid mixture a maximum absorbance value was found at a pH of 10.6. At this stage it was decided that, to reduce the complexity of the procedure, extraction with acetic acid would be abandoned, and sulphuric acid (0.8*M*) used instead.

When 0.8*M* sulphuric acid was used to extract a vulcanised sample, a precipitate formed immediately upon the addition of the colourimetric reagent. This was filtered off and analysed for zinc by atomic absorption spectroscopy. A value of 7.3% zinc was obtained. Zinc hydroxyquinolate has a zinc content of 6.9% when pure and is also a greenish-yellow colour, suggesting that this is the precipitating species. Obviously this would give rise to high apparent levels of hydroxylamine unless completely removed. As it has a small but significant solubility in the reagents, it would always contribute to the observed hydroxylamine level, even when no hydroxylamine-treated rubber was present in the product.

Various complexing agents were added to the acid digestion solution which were stronger complexing agents than the 8-hydroxyquinoline. These included ethylenediamine tetracetic acid (EDTA), lactic acid and CDTA. EDTA was initially tried but the calibration curve showed a very low response to hydroxylamine (a slope of only some 25% compared with the normal calibration curve), and this was abandoned. Lactic acid was also tried; it did not affect the slope of the calibration curve and stopped the immediate formation of a precipitate. Unfortunately the precipitate was formed at the heating stage of the test. As CDTA has a stability constant with zinc greater than that for EDTA, it was then tried. The calibration curve initially showed a higher slope than the normal calibration curve and there was no precipitate formation throughout the whole procedure.

The disadvantages of using CDTA are that the calibration curve changes with the age of solution, and CDTA is not sufficiently soluble in water to overcome the precipitation of zinc. The latter problem was easily overcome as CDTA is soluble to a sufficient extent in sodium carbonate solution, at a pH value of 11. The changing calibration curve is more serious but fortunately the change is linear so allowance can be made by including a solution of known hydroxylamine concentration in the set being analysed at any given time and obtaining a correction factor by comparing its measured value against the true concentration.

The oxygen content of the solution is also important during the colour development, indeed, if nitrogen is bubbled through the solution it is possible to completely inhibit the green colour formation. Rather than relying on atmospheric oxygen to be present at a sufficient level in the solution we instituted the procedure of saturating the solution with oxygen.

In second, and subsequent extractions it is usual to find very little hydroxylamine; typically less than 10% of the level obtained from the first extraction. For this reason it is not usually necessary to carry out these further extractions, as an accurate figure is not required to show compliance, or otherwise, with the regulation.

The above factors were all taken into account in deriving the method as described for vulcanisates containing zinc. All our attempts to overcome the problems relating to calcium interference have, as yet, been to no avail. At the moment the only way to obtain a realistic hydroxylamine estimation is to prepare a vulcanisate to the same formulation with SMR L and analyse it as a control at the same time.

The effect of calcium filler was proved beyond doubt by taking a weight of Calofort S equivalent to that in the vulcanisation used, extracting with acid for 16 h, and following the hydroxylamine estimation procedure. Assuming an 'equivalent vulcanisate sample weight' of 5 g, the determined 'hydroxylamine' content was 12 p.p.m.

Results Obtained from Vulcanisates

Table 1 shows the recipes and cure times used to prepare a range of samples for testing as described in the second method and *Table 2* gives the results obtained for those materials. Included in *Table 2* are results obtained for the

TABLE 1. MIXES USED IN HYDROXYLAMINE DETERMINATIONS

Item	Mix									
	1	2	3	4	5	6	7	8	9	10
SMR CV	100	100	100	100	100					
SMR GP						100	100	100		
SMR L									100	100
Zinc oxide	5	5	5	5	5	5	5	5	5	5
Stearic acid	1.5	1.5	1.5	1.5	2.0	1.5	1.5	1.5	2.0	2.0
CBS	0.5	0.5	5.0	0.5			0.5			
Robac P25					0.5	0.5		0.5	0.5	0.5
TMTM					0.2			0.2	0.2	0.2
S	2.5	2.5	0.3	2.5	2.5	2.5	2.5	2.5	2.5	2.5
Calofort S					50			50	50	
N550 black				40			50			
Flectol H		2	2	2	2		2	2	2	2
Dutrex 729		3	3	10	5		10	5	5	5
Mix type/cure system	ACS 1	Conv.	EV	Conv. Black	Conv. White	GP ACS1	Conv. Black	Conv. White	SMR L Conv. white	Conv.
Cure temp. (°C)	150/180	140/180	140/180	140/180	150	150	150	150	150	150
Cure time (min)	30/4	$45/4^{1}/2$	90/12	$40/3^{3}/4$	20	20	20	20	20	20

TABLE 2. HYDROXYLAMINE RECOVERED FROM MIX

Mix	Hydroxylamine recovered (p.p.m.)				
	Raw rubber (first method)	Raw rubber compounded	Vulcanised rubber cured at		
			140°C	150°C	180°C
1	64	22	-	2	ND
2	61	23	ND	-	ND
3	65	20	ND	-	ND
4	70	5	ND	-	ND
5	70	37	-	12	-
6	165	38	-	ND	-
7	160	20	-	ND	-
8	170	35	-	14	-
9	ND	17	-	9	-
10	ND	ND	-	ND	-

ND = none detected — below detection limit of 2 p.p.m.
\- = no determination carried out

analysis of the raw rubbers and raw compounded rubbers.

Of *Mixes 1–5,* where SMR CV is the elastomer, only *Mix 5, which contains Calofort S,* shows any residual hydroxylamine after vulcanisation. This result, however, should be compared with that for *Mix 9* where the SMR CV is replaced with SMR L. The SMR CV vulcanisate contains only 3 p.p.m. hydroxylamine more than the SMR L mix (where no hydroxylamine is present). Under the conditions of analysis, where the detection limit is 2 p.p.m. this is not considered significant. In *Mixes 6–8,* where SMR GP has been used, only *Mix 8* shows any hydroxylamine, and, after allowing for the 'blank' *(Mix 9),* it could have a trace present. *Mix 10* shows that hydroxylamine is not found in an SMR L vulcanisate if that mix contains neither hydroxylamine nor calcium but *Mix 9* shows that the presence of a calcium filler at 50 p.p.h.r. leads to an apparent hydroxylamine level of about 9 p.p.m. Although these data suggest that it would be valid to conclude that all the hydroxylamine which appears to be present in mixes containing calcium-containing fillers is an artifact resulting from the filler, we currently have no means of complexing the calcium when present and thus are not able to remove the artifact.

CONCLUSION

A method has been developed which allows the accurate determination of hydroxylamine in black-filled vulcanisates based on CV rubber, provided that they do not contain significant levels of calcium salts which might be extracted with 0.8*M* sulphuric acid.

During the development of this method, the validity of the unpublished procedure for estimating hydroxylamine in raw NR-CV was confirmed, and the opportunity was taken to present them together.

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