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# *Viscosity Stabilisation of Natural Rubber with Semicarbazide Hydrochloride*

ONG CHONG OON

*Commercially available viscosity-stabilised rubbers are darker in colour and slightly slower-curing than the corresponding SMR 5L. A process has now been developed to produce a viscosity-stabilised rubber with raw and vulcanisate properties equivalent to SMR 5L. The influence of some of the more important processing variables are also examined.*

Viscosity-stabilised natural rubber (CV) is commercially produced by treating latex with a small dosage of a hydroxylamine salt. The main benefit of using such a rubber is in savings accrued by the elimination of the mastication step during primary processing operations (ALLEN *et al.*, 1971). However, it has disadvantages of being slightly slower curing and darker in colour than the corresponding SMR 5L grade (CHIN, 1969).

This paper discusses the production of a light-coloured version of viscosity-stabilised rubber (CVL).

## EXPERIMENTAL

### *Preparation*

The method of preparation of CVL is similar to that of the CV rubber (CHIN, 1969) except that semicarbazide hydrochloride (0.4% weight on rubber) is substituted for the hydroxylamine salt.

Field latex is sieved through a 40 mesh sieve. The minimum amount of ammonia as latex preservative is used and added within the range of 0 % to 0.05% on the latex. The required amount of castor oil is stirred into the latex either directly or by a plunger-masterbatch method. This is followed by a 5% aqueous solution of sodium metabisulphite (0.04% by weight on the rubber) to prevent enzymic darkening. While keeping the latex mixture well stirred, 10% aqueous solution of semicarbazide hydrochloride (0.4% by weight on the rubber) is added and stirring is continued for about 3 minutes. The latex is then coagulated with 2% formic acid. The coagulum is left to mature for 8 – 10 h before being reduced to crumbs. The crumbs are then dried by hot air circulation at temperatures set between 100 – 110°C.

## RESULTS AND DISCUSSION

### *Effect of Processing Variables*

*Preservation.* Latex, when cannot be processed immediately after collection, needs to be preserved. The commonest preservative is ammonia and the amount required is dependent on the period of preservation. The effect of overnight preservation with 0.2% ammonia is illustrated in *Figure 1* and *Table 1*. Latex preserved overnight requires a higher concentration of semicarbazide hydrochloride to pass the CV test. The rubber is also darker in colour. It is therefore advisable to use latex which has been preserved for a short period in the production of CVL rubber.

*pH of coagulation.* Since the reaction of semicarbazide hydrochloride with an aldehyde is a condensation reaction known to be acid catalysed, it was expected that the pH of coagulation would have an influence

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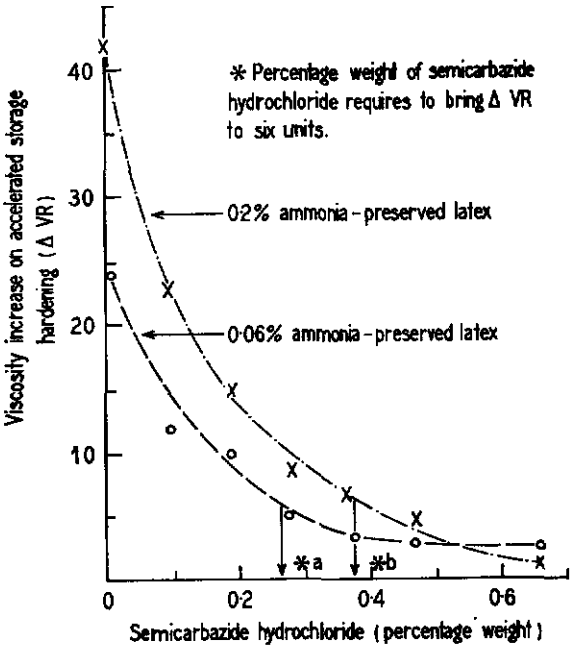


*Figure 1. Effect of preservation*

on the efficiency of reaction. *Figure 2* illustrates the negative effect of the pH of coagulation within the range of 4.5 to 5.5, the range normally encountered in a new process factory. This is fortunate as the pH of coagulation is difficult to precisely control in a large factory.

*Drying temperature.* Although the drying temperature of 100°C is recommended for SMR factories, some factories dry their rubber at temperature set between 110 – 120°C. The drying temperature for a new rubber is therefore an important consideration. The negative effect of a drying temperature within the range of 90 – 120°C is amply demonstrated in *Figure 3.* This can be attributed to the stability of semicarbazide hydrochloride (decomposition temperature 173°C).

*Concentration. Figures 1, 2* and *3* show that the concentration of semicarbazide hydrochloride required for satisfactory production of the CVL rubber varies from 0.21% to 0.37%. After allowing for the accuracy in the method of estimating d.r.c. and the measurement of the volume of

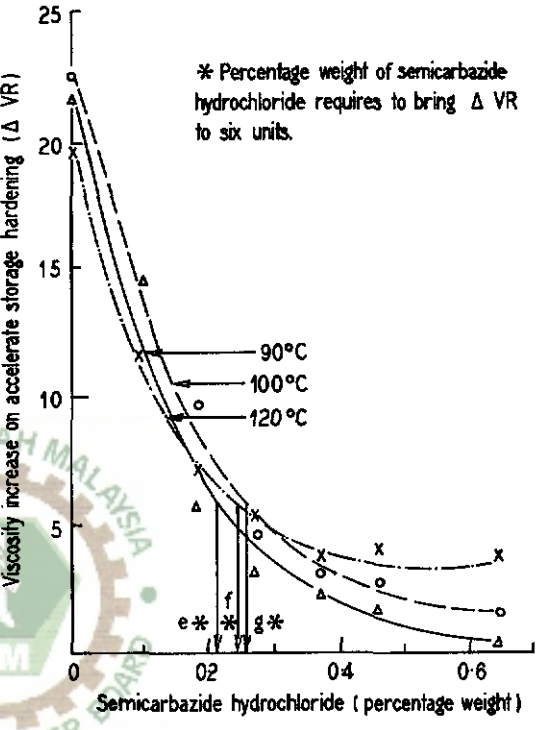


*Figure 2. Effect of pH of coagulation*

TABLE 1. EFFECT OF LONG PERIOD OF PRESERVATION OF LATEX ON CVL RUBBER

| Period of preservation (h) | Ammonia contents of latex (%) | Colour (Lovibond unit) | Increase in Mooney viscosity after accelerated storage hardening $\triangle V_R$ |
|---|---|---|---|
| 0 | 0 | 5 (3.5) | ½ (28) |
| 0 | 0.03 | 5 (3.5) | 1½ (28) |
| 16 | 0.23 | 8 (8.0) | 4 (43) |

Figures within brackets refer to the control rubber.



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latex for large-scale preparation, a concentration of 0.4% weight on rubber of semi-carbazide hydrochloride is recommended for the large-scale production of the CVL rubber. This was found to be adequate in five semi-factory and eight factory-scale trials conducted at the RRIM Experiment Station factory. One semi-factory-scale trial included modification in the pH of coagulation, drying temperature, coagulum and crumbs maturation. The results are presented in *Tables 2, 3* and *4*.

*Properties of Rubbers*

*Raw rubber properties.* The raw rubber properties are given in *Tables 2* and *3*. A summary of the data is given below.

- All the rubbers are within the SMR specifications for the top grade rubber.
- CVL rubbers are comparable to their control in colour but CV rubbers are darker in colour.
- The Mooney viscosity of the rubbers follows the order control>CVL>CV.

TABLE 2. TYPICAL RAW RUBBER PROPERTIES FOR SEMI-FACTORY-SCALE TRIALS

| Property | Control | CV rubber | CVL rubber |
|---|---|---|---|
| Dirt (% wt) | 0.009 | 0.005 | 0.010 |
| Ash (% wt) | 0.22 | 0.21 | 0.21 |
| Nitrogen (% wt) | 0.41 | 0.41 | 0.39 |
| Volatile matter (% wt) | 0.25 | 0.24 | 0.28 |
| Mooney viscosity ML 1 + 4′@ 100°C | 71¾ | 59¼ | 66¼ |
| PRI | 85 | 94 | 90 |
| $\triangle V_R$ | 14¼ | 2¼ | 4½ |
| Colour (Lovibond unit) | 5 | 8.0 | 5 |
| Initial Wallace plasticity (Po) | 44.5 | 36 | 40 |
| MOD value | 5.9 | 5.3 | 5.8 |
| Acetone extract (% wt) | 3.65 | 3.70 | 3.69 |

TABLE 3. TYPICAL RAW RUBBER PROPERTIES FOR FACTORY-SCALE TRIALS

| Property | Control | CV rubber | CVL rubber |
|---|---|---|---|
| Dirt (% wt) | 0.004 | 0.008 | 0.005 |
| Ash (% wt) | 0.22 | 0.22 | 0.21 |
| Nitrogen (% wt) | 0.44 | 0.44 | 0.44 |
| Volatile matter (% wt) | 0.19 | 0.22 | 0.17 |
| PRI | 97 | 95 | 95 |
| Mooney viscosity ML 1 + 4′@ 100°C | 68¾ | 58½ | 64¾ |
| $\triangle V_R$ | 22¼ | 4½ | 4 |
| Colour (Lovibond unit) | 3.5 | 7.0 | 5.0 |
| Initial Wallace plasticity (Po) | 45 | 37 | 42 |
| Mod value | 6.1 | 5.4 | 6.0 |

TABLE 4. EFFECT OF MODIFICATION IN PROCESSING

| | pH of coagulation | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 4.5 | | | | | | | | | | | | | | | | | | 5 | | | | | | | | | | | | | | | | | |
| | Drying | | | | | | | | | | | | | | | | | | Temperature | | | | | | | | | | | | | | | | | |
| | 100°C | | | | | | | | | | | | 120°C | | | | | | 100°C | | | | | | | | | | | | 120°C | | | | | |
| | Coagulum | | | | | | | | | | | | | | | | | | Maturation | | | | | | | | | | | | | | | | | |
| | 0 h | | | 24 h | | | 48 h | | | 0 h | | | 24 h | | | 48 h | | | 0 h | | | 24 h | | | 48 h | | | 0 h | | | 24 h | | | 48 h | | |
| | Crumb | | | | | | | | | | | | | | | | | | Maturation | | | | | | | | | | | | | | | | | |
| | 0 h | 24 h | 48 h | 0 h | 24 h | 48 h | 0 h | 24 h | 48 h | 0 h | 24 h | 48 h | 0 h | 24 h | 48 h | 0 h | 24 h | 48 h | 0 h | 24 h | 48 h | 0 h | 24 h | 48 h | 0 h | 24 h | 48 h | 0 h | 24 h | 48 h | 0 h | 24 h | 48 h | 0 h | 24 h | 48 h |
| Mooney viscosity ML 1+4′ @ 100°C | 57 | 57½ | 55 | 57½ | 55½ | 55½ | 56½ | 56 | 55½ | 60 | 58½ | 58½ | 58 | 58½ | 57 | 58½ | 59½ | 56½ | 58½ | 56½ | 56 | 56 | 57 | 56½ | 56 | 56½ | 57½ | 59½ | 60½ | 57½ | 60 | 60½ | 59½ | 57 | 59½ | 60 |
| $V_R$ | 2 | 3 | 3½ | 1½ | 2½ | 3½ | 3 | 4 | 2 | 4¾ | 4½ | 4½ | 4¾ | 3 | 3½ | 3½ | 2 | 2½ | 2½ | 3 | 2½ | 2½ | 2½ | 2 | 1½ | 2 | 2 | 3¼ | 2¼ | 3 | 2¾ | 3¼ | 3¼ | 3 | 3¼ | 3¾ |

CVL rubbers are about 6 Mooney units higher than the corresponding CV rubbers. This feature of CVL rubbers is advantageous for the preparation of viscosity-stabilised rubber from the new high-yielding clones which generally give low viscosity rubbers.

*Vulcanisate properties.* For ACS 1 mix, CVL rubber is found to be faster curing than the corresponding CV rubber and equivalent to the corresponding control. This is shown on rheometer *(Table 5)* and MOD data given in *Tables 2* and *3*. As consequence of the faster curing characteristics, CVL and the corresponding control rubbers have higher tensile strength, modulus, resilience and hardness at a given time than those of the corresponding normal CV rubber. However, ageing characteristics of CV rubber is slightly superior to the corresponding CVL and control rubber *(Table 6)*. This could have been due to the slower curing behaviour of CV rubber since the ageing effect can be counteracted by continuation of cure under the ageing conditions.

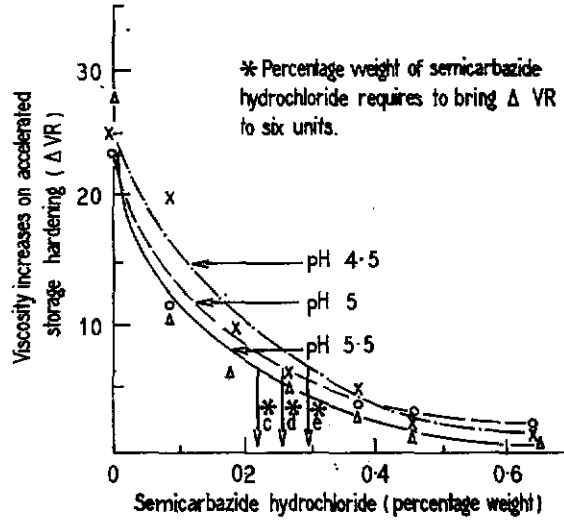


*Figure 3. Effect of drying temperature*

For tread mix, mixing, curing and vulcanisate properties of CVL rubber are comparable to the corresponding control and CV rubbers *(Tables 7 and 8)*.

TABLE 5. ACS–1 MIX COMPOUNDING AND CURING CHARACTERISTICS

| Sample reference | Control | CV | CVL |
|---|---|---|---|
| Curring characteristis | | | |
| Mooney viscometer Vc (ML 1 + 4′@ 100°C) | 49 | 42 | 46 |
| Scorch time (min. to 5 pt. rise @ 120°C) | 9.8 | 17.2 | 12.2 |
| Monsanto Rheometer | | | |
| Starting conditions: HS Temp = 190°C; Range = 50; Chart motor = 12″; Pre-heat time = 20″ | | | |
| Minimum viscosity, T min (in lb) | 17.8 | 15.7 | 16.1 |
| Scorch time, $t_2$ (min) | 3.5 | 4.4 | 2.5 |
| Maximum torque T max (in lb) | 32.8 | 29.4 | 32.9 |
| Optimum torque, $T_{90}$ (in lb) | 31.3 | 28.0 | 31.2 |
| Optimum cure time, $t_{90}$ (min) | 9.7 | 8.6 | 6.0 |
| Cure ratet $_{90} - t_2$ (min) | 6.2 | 4.2 | 3.5 |
| $\Delta$T | 15.0 | 13.7 | 16.8 |

TABLE 6A. ACS–1 MIX VULCANISATE PROPERTIES (1)

| Sample reference | Cure time (min) | Control | CV | CVL |
|---|---|---|---|---|
| Tensile strength (MN. $m^{-2}$) | 30 | 21.5 | 17.4 | 16.6 |
| | 40 | 23.1 | 14.7 | 20.5 |
| | 50 | 22.6 | 18.1 | 21.5 |
| Elongation at break (%) | 30 | 790 | 810 | 755 |
| | 40 | 800 | 780 | 790 |
| | 50 | 790 | 800 | 800 |
| Modulus at 300% (MN. $m^{-2}$) | 30 | 1.1 | 0.9 | 1.1 |
| | 40 | 1.4 | 1.0 | 1.3 |
| | 50 | 1.4 | 1.1 | 1.4 |
| Modulus at 600% (MN. $m^{-2}$) | 30 | 6.3 | 5.0 | 6.2 |
| | 40 | 6.5 | 4.7 | 6.4 |
| | 50 | 6.5 | 5.0 | 6.0 |
| Relaxed modulus, MR 100 (MN. $m^{-2}$) | 30 | 0.6 | 0.5 | 0.6 |
| | 40 | 0.6 | 0.5 | 0.6 |
| | 50 | 0.6 | 0.5 | 0.6 |
| Dunlop resilience at 20°C (%) | 30 | 84.3 | 78.8 | 82.6 |
| | 40 | 84.5 | 79.9 | 84.1 |
| | 50 | 84.5 | 80.3 | 84.3 |
| Hardness (IRHD) | 30 | 34.5 | 32.3 | 34.3 |
| | 40 | 35.1 | 33.0 | 35.5 |
| | 50 | 35.7 | 33.2 | 35.8 |

TABLE 6B. ACS–1 MIX VULCANISATE PROPERTIES (1)
(Aged results)

| Sample reference | 40 min 140°C cure | Control | CV | CVL |
|---|---|---|---|---|
| Tensile strength (MN. $m^{-2}$) | 7d/70°C | 23.6 | 24.4 | 25.4 |
| | % reten. | 102 | 166 | 124 |
| | 14d/70°C | 14.2 | 16.8 | 15.4 |
| | % reten. | 61 | 114 | 75 |
| Elongation at break (%) | 7d/70°C | 680 | 740 | 710 |
| | % reten. | 85 | 95 | 90 |
| | 14d/70°C | 570 | 610 | 580 |
| | % reten. | 71 | 78 | 73 |
| Modulus at 300% (MN. $m^{-2}$) | 7d/70°C | 1.7 | 1.8 | 1.6 |
| | % reten. | 121 | 180 | 123 |
| | 14d/70°C | 2.2 | 1.9 | 2.2 |
| | % reten. | 157 | 200 | 169 |
| Modulus at 600% (MN. $m^{-2}$) | 7d/70°C | 13.6 | 11.1 | 14.4 |
| | % reten. | 210 | 236 | 225 |
| | 14d/70°C | – | 15.1 | 15.4 |
| | % reten. | – | 321 | 241 |
| Relaxed modulus, MR 100 (MN. $m^{-2}$) | 7d/70°C | 0.7 | 0.7 | 0.7 |
| | % reten. | 117 | 140 | 117 |
| | 14d/70°C | 0.7 | 0.7 | 0.7 |
| | % reten. | 117 | 140 | 117 |

TABLE 7. TREAD MIX – COMPOUNDING AND CURING CHARACTERISTICS

| Sample reference | Control | CV | CVL |
|---|---|---|---|
| Banbury mixing details | | | |
| Starting conditions: Batch Vol = 2000 ml; Temp = 100°C; RPM = 80 | | | |
| Peak Power (KW) | 15.8 | 15.9 | 16.0 |
| DUMP temperature (°C) | 160 | 158 | 162 |
| Curing characteristics | | | |
| Mooney Viscometer VR Initial | 71 | 55½ | 62 |
| Pre-mast | 62 | – | – |
| $V_B$ (ML 1 + 4 @ 100°C) | 95 | 83 | 94⅓ |
| Scorch time (min to 5 pt. rise at 120°C) | 21.3 | 20.1 | 20.4 |
| Monsanto Rheometer | | | |
| Starting conditions: HS Temp = 140°C; Range = 100; Chart motor = 60′; Pre-heat time = 20″. | | | |
| Minimum viscosity, T min (in lb) | 24.0 | 22.2 | 24.7 |
| Scorch time, $t_2$ (min) | 11.5 | 11.3 | 11.8 |
| Maximum torque, T max. (in lb) | 71.8 | 70.3 | 72.1 |
| Optimum torque, $t_{90}$ (in lb) | 43.2 | 39.0 | 42.2 |
| Cure rate, $t_{90} - t_2$ (min) | 31.7 | 27.7 | 30.4 |
| $\Delta T$ | 47.8 | 48.1 | 47.4 |

Compound formulations:

| | | | |
|---|---|---|---|
| NR | 100 | Nomox ZA | 1.5 |
| ZnO | 4 | Nonox BL | 1.0 |
| St. Acid | 2 | Santocure NS | 0.5 |
| HAF | 50 | S | 2.5 |
| Dutrex | 5 | | |

TABLE 8A. TREAD MIX – VULCANISATE PROPERTIES (1)

| Sample | 45 min at 140°C cure | Control | CV | CVL |
|---|---|---|---|---|
| Tensile strength ($MN.m^{-2}$) | Unaged | 28.0 | 27.4 | 28.5 |
| | A 1d/100°C | 20.6 (74) | 21.1 (77) | 21.3 (75) |
| | 3d | 7.5 (27) | 8.7 (32) | 8.8 (31) |
| Elongation at break (%) | Unaged | 510 | 510 | 520 |
| | A 1d/100°C | 340 (67) | 370 (73) | 360 (69) |
| | 3d | 150 (29) | 180 (35) | 190 (37) |
| Modulus at 300% ($MN.m^{-2}$) | Unaged | 13.6 | 13.5 | 13.9 |
| | A 1d/100°C | 18.4 (135) | 17.3 (128) | 17.3 (124) |
| Relaxed modulus, MR 100 ($MN.m^{-2}$) | | 2.10 | 2.04 | 2.16 |
| Dunlop resilience at 20°C (%) | | 62.4 | 61.9 | 63.5 |
| Hardness (IRHD) | | 65.9 | 65.7 | 66.9 |

Figures within brackets denote percentage after ageing.

TABLE 8B. TREAD MIX – VULCANISATE PROPERTIES (2)

| Sample reference | 40 min at 140°C cure | Control | CV | CVL |
|---|---|---|---|---|
| Tear Strength (N per Std. test piece) | – | 330.6 | 319.9 | 306.6 |
| Akron abrasion dusted (ml. loss/1,000 rev.) | – | 0.062 | 0.062 | 0.066 |
| Flex Cracking (kc. to grade C) | – | 120<br>110 | 90<br>110 | 80<br>90 |
| Cut growth (kc)<br>2 – 4 mm<br>4 – 8 mm<br>8 – 12 mm | | <br>2.25<br>7.80<br>11.15 | <br>2.60<br>9.70<br>11.30 | <br>3.00<br>11.20<br>25.80 |
| Goodrich Flexometer (Heat build-up)<br>Starting condition: M/C 2 Stroke = 0.175 in; Applied load = 30 lb | | | | |
| Temp. (°C) rise after 25 min | +5′ | 32 | 34 | 34 |
| Temp. (°C) rise after 60 min | | 44 | 48 | 44 |
| Permanent set (%) | | 16.2 | 17.9 | 16.8 |
| Dynamic compression set (%) | | 12.1 | 14.5 | 13.2 |
| Relative resilience (%) | | 67.0 | 63.8 | 65.6 |
| Compression set (%) | | 8.1 | 8.1 | 8.1 |
| (72 h at 20 ± 2°C) 30′ rec. | | | | |

## CONCLUSION

Viscosity-stabilised natural rubber can be prepared by the addition of semicarbazide hydrochloride to the latex prior to coagulation. Besides being viscosity stabilised, semicarbazide hydrochloride stabilised rubber is light in colour and has cure rate equivalent to SMR 5L grade. Therefore, it can be used in the manufacture of light-coloured products. The low toxicity of semicarbazide hydrochloride presents no handling problem in the process factory. It also permits the use of semicarbazide hydrochloride viscosity-stabilised rubber for the manufacture of products for the packaging of food.

The cost of production of semicarbazide hydrochloride viscosity-stabilised rubber is estimated at 4.7 ct (M) per kilogram compared to 0.6 ct (M) per kilogram for normal CV rubber. This is attributed to the high cost of semicarbazide hydrochloride (M$5.60 per pound compared to M$1.70 per pound for hydroxylamine neutral sulphate), as well as to the higher concentration required (0.4% on rubber compared to 0.15% on rubber for hydroxylamine neutral sulphate).

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