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Highly Purified Natural Rubber IV. Preparation and Characteristics of Gloves and Condoms

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Rubber gloves were produced using highly deproteinised natural rubber (HDPNR) latices with green strength comparable to that of gloves produced from a commercial high-ammonia natural rubber (HA) latex These latices were prepared from HA latex by the method previously reported The prevulcanisation of HDPNR latex gave characteristics which are slightly different from those of HA latex, although it did not affect the glove preparation process The HDPNR gloves thus prepared (except chlorinated ones) satisfied the ASTM *specifications for examination gloves and were superior to the gloves from HA latex in terms of softness, clarity and low odour Condoms also were prepared from two different types of HDPNR latex; one was the above mentioned HDPNR latex and another was a HDPNR latex prepared from a prevulcanised HA latex The condoms from these HDPNR latices were superior to those from HA latex in terms of softness, transparency, water resistance and lack of odour*

Ever since it was recognised that the residual extractable proteins in natural rubber (NR) latex products caused the Type 1 allergy, the development of low allergen products has been strongly requested for medical and hygienic rubber articles such as surgical gloves, examination gloves, condoms, *etc* [1]

In the range of medical gloves, some hypo-allergenic gloves have been produced The use of doubly centrifuged NR latex and techniques reducing extractable proteins such as leaching and chlorination have been employed in the commercial production of these gloves

Recently some progress has been achieved in this area First, the use of newly developed re-centrifuged prevulcanised NR latex that could achieve apparently lower level of the residual extractable proteins compared with previous techniques[2] Second, the use of deproteinised NR (DPNR) latex. Production test on examination gloves was carried out using DPNR latex containing 0 06% - 0.1% nitrogen[3].

A new highly deproteinised NR (HDPNR) latex also was successfully developed whose nitrogen content was found to be less than 0.02%[4 5]. In the previous reports of this series,

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a HDPNR latex having excellent physical properties and processability was described and it was claimed that the HDPNR latex would be safer than conventional NR latex which was known to cause Type 1 allergy reaction because antibody was detected in the serum of animals sensitised with the latter but not with the former[6-8].

In this report, the results are presented for producing gloves and condoms from HDPNR latex having high green strength.

EXPERIMENTAL

Preparation of HDPNR Latex

HDPNR A. The commercial HA latex, diluted with water to 30% dry rubber content (DRC), was mixed with 0.02% (w/v) of a proteolytic enzyme (KP-3939, Kao Co.) and 1% (w/v) of a surfactant (KP-4401, Kao Co.), and the mixture was incubated for 24 h at room temperature under slow stirring. The reacted mixture was diluted with water to 10% DRC, then centrifuged (Alfa Laval) to obtain 60% DRC latex (A1). The washing procedure was repeated once more to obtain the latex A2. The concentration of ammonia in the latices was adjusted to 0.3% (w/v).

HDPNR B. The commercial HA latex was mixed with 0.5 p.h.r. accelerator, 1.0 p.h.r. sulphur, 1.0 p.h.r. ZnO and 0.5 p.h.r. antioxidant, and then prevulcanised for 15 h at 50°C. The prevulcanised latex was diluted with water to 30% DRC and then mixed with 0.02% (w/v) of the proteolytic enzyme (KP-3939, Kao Co.) and 1% (w/v) of the surfactant (KP-4401, Kao Co.), and the mixture was incubated for 24 h at room temperature under slow stirring. The reacted prevulcanised latex was washed twice using the same procedure as above. Also the ammonia concentration of the latex was adjusted to 0.3% (w/v).

Some properties of HDPNR latices prepared for the present work are shown in *Table 1*.

Compounding

The compound formulation for producing gloves consisted of 0.6 p.h.r. – 1.0 p.h.r. accelerator, 1.0 p.h.r. sulphur, 1.0 p.h.r. ZnO and 0.5 p.h.r. antioxidant.

TABLE 1. SOME PROPERTIES OF HDPNR LATICES

Kind of latex	A1	A2	B	C
N content (%)	0.030	0.013	0.014	0.30
Viscosity (cps)	60	65	60	100
Mechanical stability time (sec)	700	550	240	1 100
Gel fraction (%)	16	15	100	60
Green strength (MPa)	4.9	5.0	–	5.5

Note: 1. Latices A1, A2 and B (please see text)
2. Latex C is a commercial HA latex employed as a control.

Maturation of Latex Compound and Curing of Latex Film

The latex compound was stood at 30°C under slow stirring. After each maturing period, dry unvulcanised film was prepared from it by the method described in the previous paper[5]. The dry rubber film was vulcanised in a circulating hot-air oven at 100°C for 1 h.

Production of Gloves

The HDPNR gloves were produced in a coagulant dipping process as shown in *Figure 1*.

Production of Condom

Condoms were produced in a straight dipping process as shown in *Figure 2*. The thickness of condoms was adjusted to 0.06 mm.

Evaluation of Physical Properties

Viscosity and mechanical stability (MST) of latex concentrates were determined according to *JIS K6381-82*.

Gel fraction and green strength of HDPNR were determined by the method described in the previous paper[5].

Evaluation of physical properties such as tensile strength (TS), elongation-at-break (EB), modulus at 300% extension (M300), modulus at 500% extension (M500) and modulus at 800% extension (M800), and tear strength were carried out according to procedures set out by *JIS K6301-75, JIS T9107-92* and *JIS T9111-85*.

Total nitrogen-content was determined by the Kjeldahl method.

Residual extractable protein content was determined by the Lowry microassay according to *ASTM D5712-95*.

Absorption of water and of toluene were determined after film specimens were soaked in either of the liquids for 24 h at 40°C.

Amount of $KMnO_4$ consumed by the extractable reducing ingredients ($KMnO_4$ value) was determined as follows: 1.5 g condom specimens were boiled with 150 ml water for 30 min. 150 ml test solution was prepared by addition of water to the above extracted solution. 10 ml 0.01 *N* $KMnO_4$ solution, 0.1 g KI and 5 drops of starch indicator were added into 10 ml test solution. The mixture was boiled for 3 min and was cooled. Then, it was titrated with 0.01 *N* $Na_2S_2O_3$ solution to determine the consumed amount of $KMnO_4$ solution.

The transparency of condoms was observed by visual comparison of each sample. The odour of condoms was judged by smelling each sample, after ageing for 7 days at 70°C.

Air-bursting test for condoms was carried out according to *ASTM D 3492-93*.

RESULTS AND DISCUSSION

Effect of Maturation of Latex Compound on Physical Properties of Vulcanisate

Tensile properties of products are frequently affected by the state of prevulcanisation of the latex compound. In this study, the effects of maturation time on physical properties of vulcanisates were investigated. In the case of HDPNR latex, modulus was found to be increased when the latex compound was

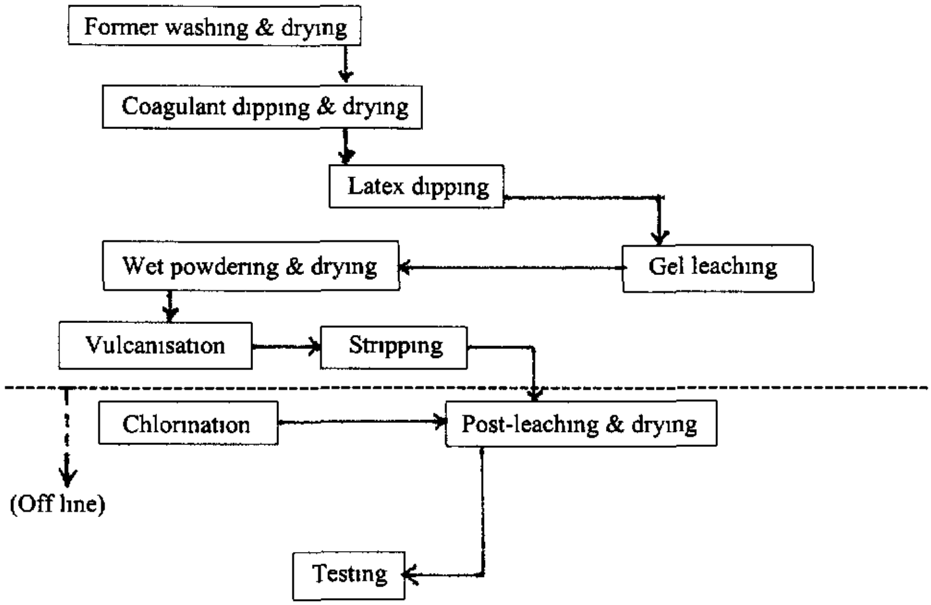

Figure 1 Process for the production of gloves.

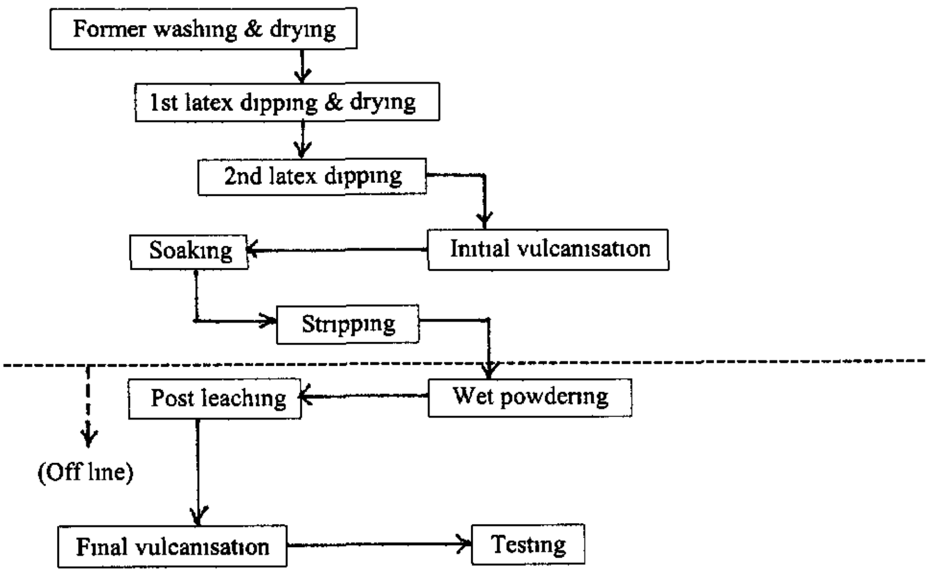

Figure 2 Process for the production of condoms

matured longer whereas tensile strength was not so much affected. In contrast, in the case of commercial HA latex, tensile strength was found to be decreased as the maturation time was lengthened whereas modulus was less affected (*Figures 3* and *4*).

These results indicate that the prevulcanisation rate of HDPNR latex is slower than that of NR latex.

Properties of HDPNR Gloves

The tensile properties of the HDPNR gloves are as shown in *Table 2*. The tensile properties of all gloves (except chlorinated ones) were well beyond the minimum requirements of *ASTM* standards for examination gloves.

The chlorinated HDPNR gloves showed too poor physical properties after ageing. It is well known that chlorination causes physical deterioration of thin gloves and results in the gloves having poor physical properties particularly after high temperature ageing at 100°C for 22 h[9,10].

Furthermore, we consider that in HDPNR, the absence of bound protein exposes the rubber chains to attack by chlorine more easily The experimental conditions for chlorination used in our work were conventional for examination gloves from HA latex but our results indicate that more careful control of the extent of chlorination may be necessary in the case of HDPNR gloves

The extractable protein (EP) contents were found to be below the sensitivity limit of the Lowry method as shown in the bottom row of *Table 2*.

The HDPNR gloves were soft and comfortable to wear owing to their lower modulus. Further, HDPNR gloves had clear colour and less odour than the gloves of HA latex. The best gloves in terms of clarity and odour were those made from the A2 latex that was prepared by double washing after the incubation with the proteolytic enzyme.

Properties of HDPNR Condoms

The tensile properties of the HDPNR condoms were as shown in *Table 3* and the stress-strain curves for the vulcanised films were as shown in *Figure 5*.

Marked differences in physical properties between M300 and M500 were found on condoms produced from HDPNR latices and those from HA latex. The condoms from HDPNR latices were clearly softer than those from HA latex, showing about half the stress values.

Some other general properties were as shown in the lower columns of *Table 3*. The total nitrogen content of the condom produced from the latex B was the lowest. In the case of the latex B, as surplus chemicals were removed during centrifuging which was carried out after the latex compound was matured for prevulcanisation, the total nitrogen content of product was reduced to the lower level. The residual extractable protein contents of HDPNR condoms were below the sensitivity limit of the Lowry method.

Further, judging from $KMnO_4$ value, the HDPNR condoms seem to have contained less amount of reducing extractable ingredients. The HDPNR condoms proved to have high water resistance as shown by their relatively low water absorption which was related to removal

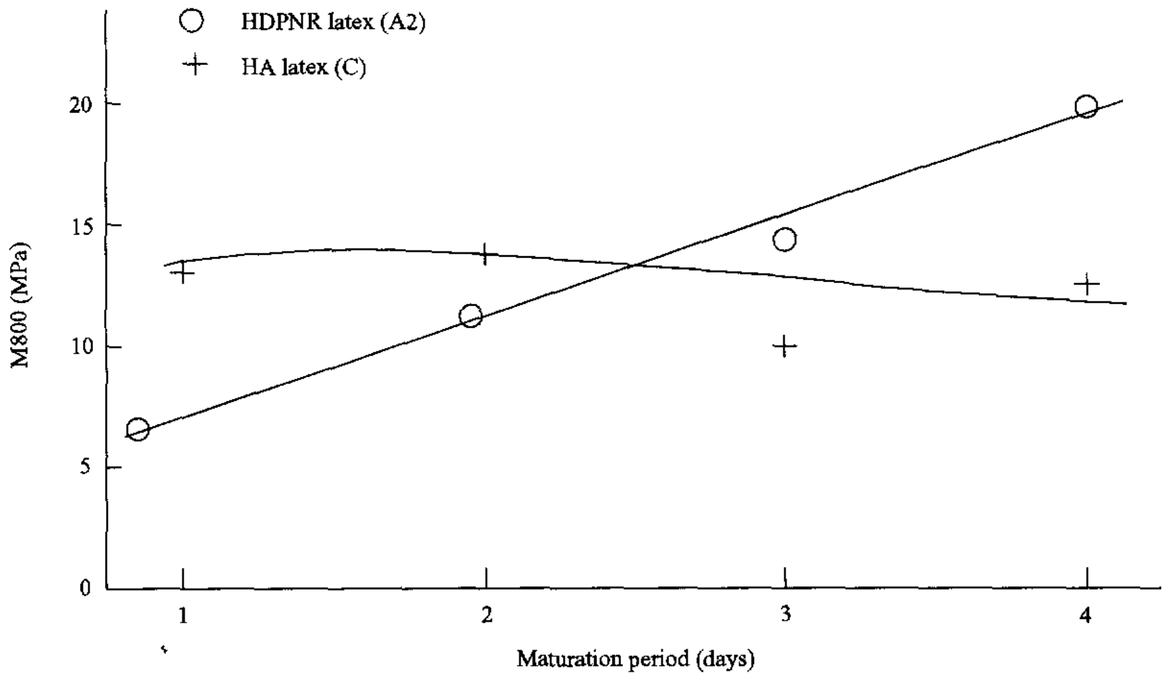

Figure 3. Maturation effect of latex compound on modulus of vulcanisate.

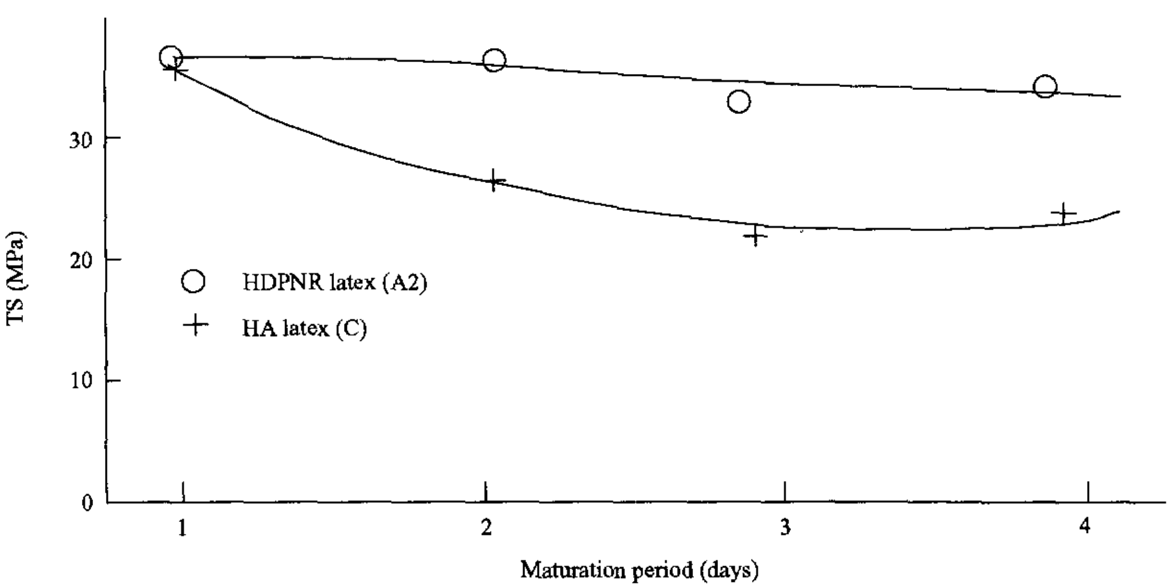

Figure 4. Maturation effect of latex compound on tensile strength of vulcanisate.

TABLE 2 TYPICAL PROPERTIES OF HDPNR GLOVES

No	1	2	3	4	5
Specification					
Kind of latex	A1	A1	A1	A2	A2
Post-leaching	No	Yes	Yes	No	Yes
Powdering	s	s	cl	s	s
Colour	A little yellowish	A little yellowish	Yellow	Colourless	Colourless
Odour	Moderate	Moderate	Little	Little	Little
Unaged					
M500 (MPa)	2.38	2.40	2 18	1.69	1 99
TS (MPa)	28.8	30 7	30.6	33.2	33.3
EB (%)	895	908	917	999	964
Aged at 100°C for 22 h					
M500 (MPa)	1 85	1.73	0 89	1.31	1 43
TS (MPa)	29.7	29.0	6.4	21.5	33.3
EB (%)	969	972	1 063	1 043	964
EP (μ g/g)	<50	<50	<50	<50	<50

Note: 1. Latices A1 and A2 (please see text)
2 s Corn starch; cl· Chlorination; EP· Extractable protein content
3. M500 for unaged gloves of HA latex is usually in 2.0 MPa to 2.4 MPa range
4. *ASTM minimum requirements for TS and EB are 21 MPa and 700% before ageing and* 16 MPa and 500% after ageing.

of hydrophilic ingredients including protein The HDPNR condoms were more transparent and had less odour than the condoms of HA latex. The condom from the latex B was particularly transparent.

The stress-strain curves obtained in air-bursting test on condoms were as shown in *Figure 6*. The HDPNR condoms proved to have air bursting volume which was more consistent and larger than that of the condoms of HA latex.

CONCLUSION

HDPNR latices have good mechanical properties and processability for producing examination gloves in the coagulant dipping process; the gloves also have low levels of EP content as well as such advantages as less

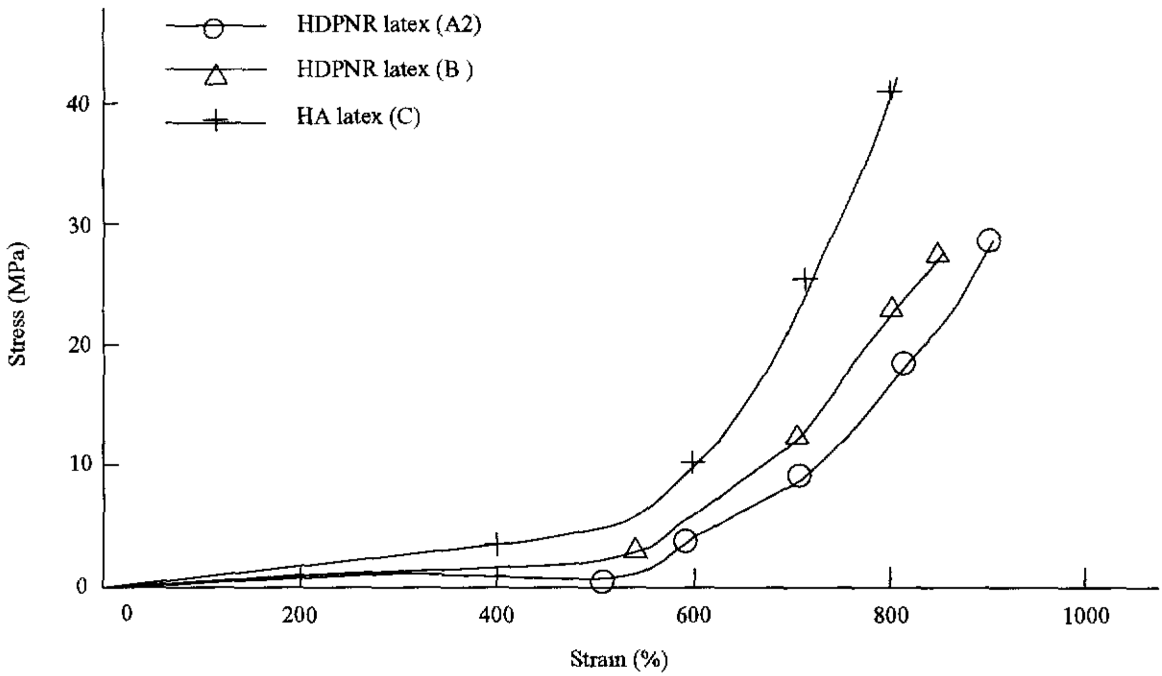

Figure 5. Stress-strain curves of vulcanised films.

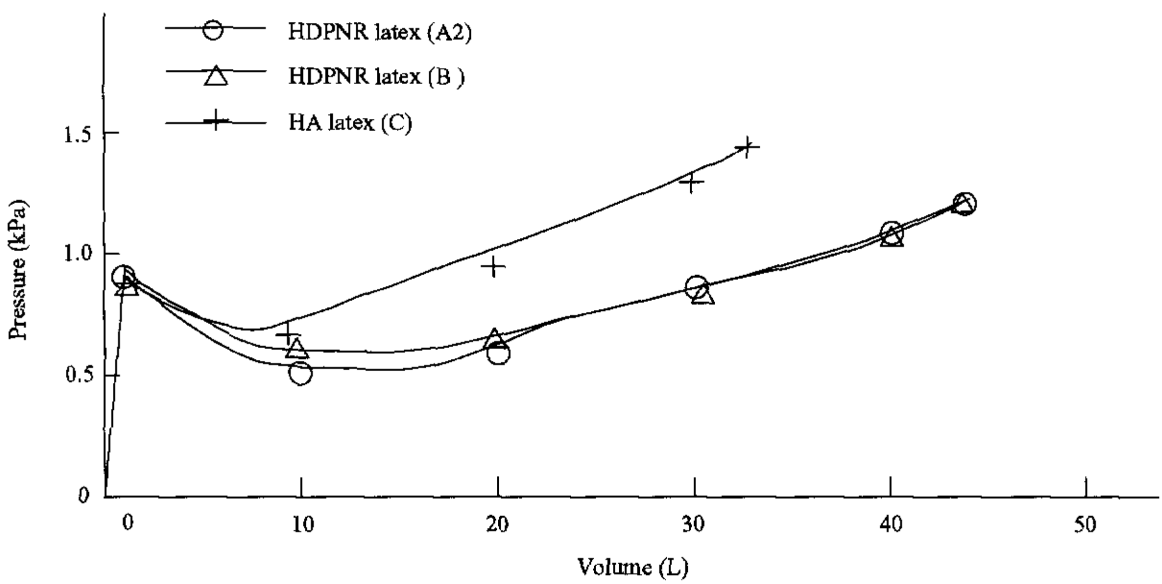

Figure 6. Air-bursting test curves of condoms.

TABLE 3. TYPICAL PROPERTIES OF HDPNR CONDOMS

Kind of latex	A2	B	C
Tensile properties			
Unaged			
M300 (MPa)	1.26	1.12	2.24
M500 (MPa)	1.90	2.24	6.71
TS (MPa)	34.0	32.8	36.0
EB (%)	933	875	863
Tear strength (kN/m)	45.0	62.5	63.3
Aged at 70°C for 10 days			
TS (MPa)	29.5	29.8	33.1
EB (%)	920	850	775
Total N content (%)	0.037	0.014	0.156
EP (μ g/g)	< 50	< 50	150
$KMnO_4$ value (ml)	0.25	0.50	0.80
Water absorption (%)	4.10	0.61	8.50
Toluene absorption (%)	414	431	393
Transparency	Good	Very good	Bad
Odour	Little	Little	Much

Note: Latices A2 and B --- (please see text)
Latex C is a commercial HA latex employed as a control.

odour, clarity in colour, and comfortable wearing feel. HDPNR latices are also good in mechanical properties and processability to produce condoms in the straight dipping process; the condoms also have low levels of EP content as well as advantages such as less odour, excellent transparency, softness, high water resistance and high burst volume. Especially, the HDPNR latex, gave the most transparent products among all latices evaluated.

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