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Accelerator Free Fact or Fiction

How accelerator-free are your gloves?

With the current media interest in Natural Rubber Latex Allergy (also known as Immediate Type Hypersensitivity, Protein Allergy or Type I), it was possibly only a question of time before the focus moved also to Allergic Contact Dermatitis (also known as Type IV, Delayed Hypersensitivity or Chemical Allergy).

Indeed with 12%[1] of the population potentially affected by allergic contact dermatitis, compared to 0.8% and 7% of the general population for Natural Rubber Latex Allergy[2], there is possibly much to be gained from minimizing the risk of Allergic Contact Dermatitis. However it should be noted that the seriousness of the symptoms associated with Allergic Contact Dermatitis are not comparable to those for Natural Rubber Latex, which may explain the level of interest being given to Natural Rubber Latex in the workplace.

> "without these chemical accelerators many of the qualities that we seek in natural rubber latex and most synthetic gloves would not be present"

In response to the growing interest in Allergic Contact Dermatitis, several glove manufacturers have introduced accelerator-free products. Chemical accelerators such as thiazoles, thiurams and dithiocarbamates are known contact sensitizers. They are used widely in the manufacture of natural rubber latex, nitrile and neoprene gloves. Indeed they often play a vital role in the vulcanization process. Without these chemical accelerators many of the qualities that we seek in natural rubber latex and most synthetic gloves (e.g. barrier performance as demonstrated by tensile strength, elasticity etc) would not be ➤

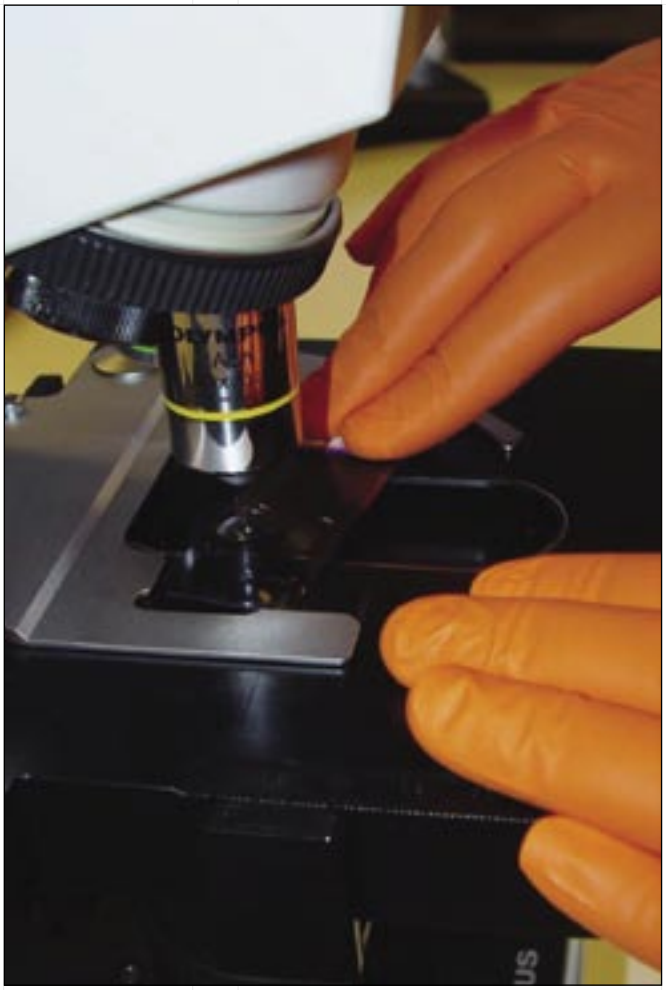
present. In addressing this issue we should be aware that over 2800 chemical agents are known to have the potential to trigger Allergic Contact Dermatitis[3] and therefore these chemical accelerators represent a relatively small proportion of the known chemical allergens. However with over 80% of reported glove-associated Allergic Contact Dermatitis being attributable to chemical accelerators[4], the removal of accelerators from gloves does offer the possibility of helping to reduce the prevalence of Allergic Contact Dermatitis.

Testing

In an effort to provide greater understanding of the value that could come from supplying accelerator-free gloves to users concerned about Allergic Contact Dermatitis, testing based on High Performance Liquid Chromatography (HPLC) and Thin Layer Chromatography (TLC) was conducted on three gloves that claim to be accelerator-free. Crucially it was hoped that a deeper insight to the basis of the accelerator-free claim would be gained.

> "most testing for residual accelerators is done through aqueous extraction using High Performance Liquid Chromatography"

These days most testing for residual accelerators is done through aqueous extraction (either distilled water or phosphate buffered saline solution extraction) using HPLC. Phosphate buffered saline solution (PBS) is often favoured, as it may better replicate the "sweaty" palm experience of the laboratory. However aqueous extraction is relatively weak and at low detection levels only MBT and MBTS are likely to be detected. As an example while the detection limit for MBT may be as low as 3ug/ml, in the case of methyl, ethyl, butyl and pentamethylene accelerator fragments this could be as high as 20 to 30 ug/ml. Likewise the choice of TLC or HPLC does have a bearing on residual accelerator analysis with each possibly favouring different types of accelerators. In recognition of the shortcomings of each



methodology, more aggressive extraction with acetone was also conducted with HPLC and TLC. Whilst it is acknowledged that acetone extraction may not be representative of the laboratory setting, it would complement the PBS extract analysis in answering the question whether accelerator-free gloves contain residual accelerators. With regard to acetone extraction, it should be noted that TLC is more sensitive to methyl, ethyl, butyl and pentamethylene accelerator fragments, whilst HPLC is more suited to MBT and MBTS. ➤

Cross reference guide to commonly used accelerators

THIURAMS	THIAZOLES	DITHIOCARBAMATES
Tetramethylthiuram Disulphide (TMTD)	Zinc Mercaptobenzothiazole (ZMBT)	Zinc Dibutyldithiocarbamate (ZDBC)
Tetramethyl Thiuram Disulphide (TMTM)	Mercaptobenzothiazole (MBT)	Zinc Dimethyldihiocarbamates (ZDMC)
Tetraethyl T hiuram Disulfide (TETD)	Benzothiazyl Disulphide (MBTS)	Zinc Diethyldithiocarbamates (ZDEC)
	Zinc Mercaptobenzimidazole (ZMBI)	Zinc pentamethylene Dithiocarbamate (ZPMC)
		Zinc Pentamethylene Dithicarbamate (ZPD)

Classes of accelerators

Methyl accelerators = ZDMC Ethyl accelerators = ZDEC Butyl accelerators = ZDBC Pentamethylene accelerator = ZPMC

Table to show detection of residual accelerators on accelerator-free gloves

MATERIAL	HPLC ON PBS EXTRACT	HPLC ON ACETONE EXTRACT	TLC ON ACETONE EXTRACT
Neoprene	None detected	None detected	None detected
Nitrile 1	None detected	None detected	Methyl accelerator fragments detected
Nitrile 2	None detected	None detected	Ethyl accelerator fragments detected

Discussion

The sample size of three accelerator-free gloves reflects the relative scarcity of these products on the market. Whilst the neoprene glove showed undetected levels of chemical accelerators even against aggressive acetone extraction, this may not mean that the gloves are entirely accelerator-free. A possible explanation is that the traditional methods for detection of accelerators were not adequate for detecting a different family of accelerators. Additional testing based on HPLC with Mass Spectrometry might provide some further clues as to the presence of accelerator fragments.

In view of the mixed results on the three accelerator-free gloves, a range of standard nitrile, neoprene and latex gloves were also tested. Some of these gloves make a claim of "Low dermatitis potential" and/or low residual accelerators, which might suggest that some testing had been carried out to support this claim.

The results once again confirm the higher level of sensitivity of TLC for detecting methyl, ethyl, butyl and pentamethylene accelerator fragments, whilst as earlier mentioned HPLC is more suited to MBT and MBTS. However if the standard method of detecting residual accelerators is used (i.e. aqueous extraction with HPLC), then only two gloves revealed accelerator fragments and not surprisingly these were MBT and MBTS. If we were to rely solely on this method, then it would appear that most of these standard gloves are little different to the accelerator-free gloves. Indeed so long as manufacturers exclude MBT and MBTS from their manufacturing process, then there may be limited prospect of aqueous extraction by HPLC detecting the presence of accelerators. ➤

Table to show detection of residual accelerators on standard gloves

MATERIAL	HPLC ON PBS EXTRACT	HPLC ON ACETONE EXTRACT	TLC ON ACETONE EXTRACT
Latex 1	None detected	Detected methyl, ethyl & butyl	Detected methyl, ethyl & butyl
Latex 2	None detected	Detected ethyl & butyl	Detected ethyl & butyl
Latex 3	None detected	None detected	Detected methyl, butyl & pentamethylene.
Latex 4	None detected	Detected either ethyl or pentamethylene	Detected either ethyl or pentamethylene.
Latex 5	None detected	None detected	Detected ethyl & butyl
Nitrile 1	MBT & MBTS detected	MBT & MBTS detected	Butyl accelerator fragments detected
Nitrile 2	None detected	Detected butyl	Detected methyl butyl & pentamethylene
Nitrile 3	MBT & MBTS detected	Detected butyl	Detected butyl
Nitrile 4	None detected	Detected ethyl	Detected ethyl
Nitrile 5	None detected	Detected ethyl	Detected ethyl
Nitrile 6	None detected	Detected ethyl	Detected ethyl
Nitrile 7	None detected	None detected	Detected ethyl
Nitrile 8	None detected	Detected butyl & MBT	Detected methyl & butyl
Nitrile 9	None detected	None detected	Detected butyl & ethyl or pentamethylene
Nitrile 10	None detected	None detected	Detected methyl & butyl fragments
Neoprene	None detected	None detected	Detected ethyl & butyl

Nitrile 9 = gloves where the manufacturers make a claim of low residual accelerators and/or low dermatitis potential

With acetone extraction, a slightly different picture emerges suggesting the use of a greater diversity of accelerators and possibly higher levels of residual accelerators. This could be because these gloves are made with a cocktail of accelerators in the manufacturing process, while for accelerator-free gloves only low levels of a single accelerator are used. Possible exceptions to this view are those gloves where residual accelerators were only detectable with TLC. Interestingly some of these are the gloves that make a low dermatitis and/or low residual accelerator claim.

Conclusion

The above analysis may reveal more questions than answers and there does seem to be case for further research being required. Whilst accelerator-free gloves may not be entirely accelerator-free, there does seem to be less use of a range of accelerators and the levels of accelerators seem to be lower. However whether these accelerator-free gloves have lower allergenic content than standard laboratory gloves (particularly those claiming low residual accelerators and/or low dermatitis potential) could merit further investigation. As allergic contact dermatitis is known to be dose and rate dependent, using gloves that are accelerator-free may have some justification in the quest to minimize its prevalence. However caution may need to be exerted in offering accelerator-free gloves to an individual that has a known sensitivity to a particular chemical accelerator. ■

References

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