## Aliphatic Amines as Diphenylguanidine Alternative for Safer and Energy-Efficient Silica-Reinforced Natural Rubber Tire Treads

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## **Abstract**

Diphenyl guanidine (DPG) can play at least two roles, i.e. as secondary accelerator and silanization catalyst, in silica-silane reinforced rubber compounds for low rolling resistance or energy-efficient tire treads. However, due to the fact that DPG can liberate toxic aniline under high mixing and processing temperatures, safe alternatives are required. This study investigates the effect of different linear aliphatic amines having varying chain lengths on the silanization efficiency of the silica/silane model system and the silica-reinforced natural rubber truck tread compounds. The amines used in this study are hexylamine (HEX-C6), decylamine (DEC-C10), and octadecylamine (OCT-C18) in comparison with DPG and with a compound without amine. The presence of all amine types in the n-decane model compound clearly increases the rate constant of the primary silanization reaction compared to the one without amine. The amine with a shorter alkyl chain gives a higher rate constant of the primary silanization reaction due to its better mobility and accessibility towards the silica surface. The results from the model study agree well with the chemically bound rubber content indicative for the extent of the silanization reaction, in additional investigated NR truck tread compounds. However, the long-chain aliphatic amines provide the shielding effect that additionally enhances the physical interactions in the rubber compounds which results in a higher total bound rubber content and better interfacial compatibility by hydrophobation between silica surface and rubber matrix. Therefore, the compound with OCT shows the lowest Payne effect and lowest heat capacity increment. The use of all amine types clearly enhances the vulcanization reaction rate compared to the one without amine. With regard to the end-use properties of rubber vulcanizates, the compound containing OCT matches the level of mechanical properties obtained by the use of DPG but shows an improved tan  $\delta$  at 60°C indicative for the tire rolling resistance.