During the Great Recession, with interest rate close to the zero lower bound, many central banks resorted to unconventional monetary policy measures with the main purpose of giving new stimulus to the real economy; however, they have also affected market uncertainty and volatility, in particular. Differently from the current literature, in which the analyses about the impact of unconventional policy on volatility are based on GARCH–type models, we propose a new model within the Multiplicative Error Model (MEM) framework. The novelty feature of our model lies in the fact that it is able to distinguish two (unobservable) volatility components: a Base component representing the autoregressive nature of volatility (following a GARCH-type model) and a Policy component, which captures the part of volatility directly depending on unconventional policies. The latter follows an AR(1) process with two exogenous variables, to capture both the announcement effect and the implementation effect of unconventional measures on volatility. We allow for unconventional policies to affect volatility both in an additive and a multiplicative, with the possibility to measure the weight of the Policy component with respect to the total level of volatility - which results to be about the 2%. By applying our model to four stock indices in the Eurozone for the period 2009-2019, we find that what matters for the effectiveness of these policies in reducing volatility is the balance sheet composition, not its size; moreover, the dampening effect of unconventional policies is more evident during the implementation of the Expanded Asset Purchase Programme, which also increases the forecasting power of our model (which is the best one if compared - through the Model Confidence Set procedure - with other models, such as the AMEM and the AMEMX). The importance of these policies is also evident from the multi-step forecast procedure, since we find that unconventional policies have reduced volatility for a maximum of 124 business days and that a further unconventional policy shock of one standard deviation would have lowered stock market volatility up to 3 points. In conclusion, this research contributes to the current debate about the suitability of unconventional monetary policy as a tool to preserve financial stability; furthermore, it could provide important information to investors for the portfolio construction process.