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Magn. Reson. Discuss., referee comment RC2
https://doi.org/10.5194/mr-2022-13-RC2, 2022

Comment on mr-2022-13

Anonymous Referee #2

Referee comment on "Mechanical ordering of pigment crystallites in oil binder: can electron paramagnetic resonance reveal the gesture of an artist?" by Elise Garel et al., Magn. Reson. Discuss., https://doi.org/10.5194/mr-2022-13-RC2, 2022

This paper is devoted to the investigation of preferential orientational distribution of crystallites of widely used copper(II) based pigment on painted surfaces using EPR spectroscopy. The underlying idea is that the orientational distribution might depend on the way the pigment has been applied on the surface, and thus EPR might be used to reveal the application technique of the pigment. The conclusions reached by the authors is that in this particular case, given the specific combination of the morphology of the crystallites and its magnetic anisotropy the method cannot provide unambiguous response, while it might be of use for pigment with different morphology.

The work is performed accurately, and the results are, as whole, sound. The subject is of interest for Magn. Reason. Discussion, and is a nice tutorial on the effect of preferential orientation on EPR spectra. However I have a major point to raise as to the general applicability of the method. Indeed, while authors performed their measurements on samples prepared on purpose, the application of the proposed method on real samples would require detachment of part of the painting to study. Does not this risk to be seen as a destructive method? A comment on this should be added in the Introduction.

A few minor points also require clarification and improvements before publication:

- Sample preparation: How were powders ground? Does the grinding procedure affect the spectra? Can authors provide an estimate of the size and anisotropy of the microcrystals they used (e.g. by the analysis of PXRD spectra)? I can imagine that the aspect ratio of the microcrystals can be modified by grinding, and this should result in different probability density as a function of the angle. This may have major consequences for the proposed method, and has to be considered.
- Linewidth: can authors think of extracting some further information from the empirical depdence of the linewidth they extracted from the analysis of their spectra? Or, seen from a different point of view: is there a reason for the chosen functional dependence

of the linewidth?

- It looks like the simulation of the spectra is much better when the orientational distribution is more isotropic: indeed, the simulated spectra for the sample magnetically oriented in fluid oil are much less convincing than the remaining ones. Authors should provide a rationale for this.
- The description of the different frames is somehow unclear: they state "the sample frame (X, Y,Z) with X, Y and Z axes having a defined position with respect to the sample." If I got it correctly from Figure 3, they mean that the sample frame (X,Y,Z) define the orientation of the sample with respect to the laboratory reference frame. This has to be clarified.
- Did authors try to use larger magnetic field to orient the fluid dispersion? It appears to me that 20 mT is quite a low field, and higher fields should result in even more pronounced preferential orientation.
- The sentence "It must also be mentioned that during the film deposition and drying, the Z-axis is along the vertical direction so that the gravitational force is perpendicular to the sample plane" is a bit misleading: it is not a matter of the orientation of the Z axis (which is a choice of the authors), but rather of the fact that the gravitational force is perpendicular to the sample plane.
- Authors state that, in case of a vertical substrate, "gravity should tend to orient the plates perpendicular to the substrate": it is however hard to see how this could happen, given the platelet form of the pigment. I can imagine an accumulation of the pigment on the low end of the substrate, but I cannot see why they should pile differently. A more detailed explanation of the reason for the expected effect should be given.