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# Examination of commercial ceramic coatings for the electrical insulation of Bi-2212 wire



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## ABSTRACT

In the last twenty years, a number of studies have been dedicated to the development of thin ceramic coating for the electrical insulation of Ag-sheathed Bi-2212 wires. Instead of preparing a coating by mixing different compounds in house, this technical note examines if commercial acrylic coatings containing  $TiO_2$  particles (white paints) could be used to form  $TiO_2$  coating on Ag-sheathed Bi-2212 wires. The compatibility of the acrylic coating with the heat treatment of Ag-sheathed Bi-2212 wire was verified by measuring the effect of coating on the critical current. It was found that the critical current is almost unaffected by the presence of the coating. The acrylic coating characteristics (for example drying time versus temperature and coating thickness at different dip coating speed) were studied and used to prepare a reel-to-reel system for coating long wires.

## 1. Introduction

Ag-sheathed Bi2223 tapes and REBCO coated conductors are supplied ready to use (i.e.: no need for heat treatment), therefore a large selection of materials can be used as electrical insulation, for example polyamide-imide coating or Kapton tape wrapping. Instead, Agsheathed Bi-2212 wires require, after winding, a partial melting heat treating (PMHT) at over 890 °C in oxygen partial pressure of 1 bar (total pressure up to 100 bar) to obtain high current density. Therefore, a material suitable for the electrical insulation of Bi-2212 wires should satisfy stringent requirements:

- being abrasion resistant and flexible, to withstand multiple bending (re-spooling) during coil fabrication.
- tolerant to high temperature (about 890  $^{\circ}\text{C})$  in oxidising atmosphere (1 bar O2 partial pressure).
- being non-reactive with the Ag sheath.
- being non-reactive with the compounds (like Cu or Bi) diffusing out from the ceramic filaments through the Ag silver sheath.

Clearly all organic (for example plastics) materials are excluded. Among inorganic materials, it has been reported [1] that E-type Glass fibre, which is used for the electrical insulation of  $Nb_3Sn$  wires, tends to

react with Ag, eventually causing or at least enlarging pinholes in Ag sheath. Only ceramic fibres (Al $_2$ O $_3$ , for example Nextel) containing less than 15 % of SiO $_2$  showed little or no reaction with Ag sheath, but these fibres are very brittle, and no braiding technique has yet been developed.

Inorganic materials as electrical insulators have been used in superconducting magnets already in 1971 [2], in the form of submicrometric  $Al_2O_3$  powder mixed with colloidal graphite, the total insulation thickness being only 13  $\mu$ m. During the 80 s and 90 s, inorganic insulation was investigated for fusion magnets, the motivation being the excellent radiation resistance of inorganic compounds compared to organic insulation materials [3]. Full inorganic insulation (mineral fibre and solution of clay and glass particles) has been introduced in 2004 [4] for  $Nb_3Sn$  cables. Recently, a commercial sol–gel paint [5] has been used to insulate REBCO coated conductors, and the winding turns were also bonded with a ceramic adhesive instead of organic epoxy; the motivation was to replace conventional organic materials with radiation resistant inorganic materials. However, this insulation system is probably not compatible with Ag-sheathed Bi-2212 wire because of the high  $SiO_2$  content.

The list of inorganic materials that have been experimentally proved to be compatible with Ag-sheathed Bi-2212 wires is very short:  $TiO_2$ ,  $Al_2O_3$ ,  $ZrO_2$  and few others [6]. For instance, alumina paper [7] has

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been used for the insulation of pancake coils wound with Bi-2212 tapes. In a similar way, MgO [8] paper has been used in the core of Rutherford cable manufactured with Bi-2212 wires. Commercial all-ceramic coatings (no organic binder) have been investigated in [9] for insulating Nb $_3$ Sn and Bi-2212 wires, but none of the coatings was found suitable for Bi-2212 wires, either because they could not withstand the heat treatment or because they resulted to be a barrier to oxygen diffusion.

During the last two decades extensive research has been carried out at the National High Magnetic field Laboratory (NHMFL), in Tallassee (USA), mainly on sol–gel thin coating. Between 2001 and 2010 [10–11], Celik et al. developed a sol–gel coating process for stabilized zirconia that was applied to Nb $_3$ Sn and Bi-2212. This process can form a 14  $\mu$ m thick layer but requires multiple coatings (between 9 and 13), and, for this reason, it was deemed economically inconvenient. Nevertheless, if compared just to the present cost of the bare wire, we think that multiple pass insulation process is unlikely to be the most expensive step in coil fabrication. One additional disadvantage was that coatings were prone to cracking because of the difference in thermal contraction between the ceramic and the Ag-sheathed Bi-2212 wire.

In 2012 [12] NHFML developed a sol–gel  $SiO_2$ - $Al_2O_3$  coating to insulate long length 316 stainless steel tape. This tape was then cowound with REBCO coated conductor into double pancakes, thus reinforcing and at the same time providing turn-to-turn electrical insulation. The  $SiO_2$  acts as an inorganic binder for  $Al_2O_3$  particles (like mortar and bricks); this coating is probably not compatible with Bi-2212 wires, because of the high  $SiO_2$  content.

In 2013 [13] nGimat (now Engi-Mat) developed a TiO2 coating, but it was not strong enough to withstand the winding process. Florida State University (FSU) took over the development of TiO<sub>2</sub> coating [14] from nGimat, aiming to replace alumina silicate (mullite) braid, which was the conventional insulation for Bi-2212. Mullite braiding has two disadvantages: 1) it has been shown [1] that fibres containing > 25 % of SiO<sub>2</sub> do react with Ag (pure amorphous SiO<sub>2</sub> does not) and in addition, Cu was found in the fibre/Ag composite after heat treatment and Cu depletion in the superconducting ceramic caused a reduction in Ic; 2) the alumina-silicate braid is rather thick (about 150 µm), and thinner insulation (about 20 to 40 µm) would increase the engineering critical current density in winding pack (up to 30 % or even 40 %, depending on the winding pack type, according to our estimates). FSU has modified the nGimat coating process by changing the chemical composition and adding an additional acrylic top coating to protect the ceramic coating during the coil fabrication process [14]; after the decomposition of the organic binder, the ceramic coating was porous and permeable to oxygen. However, it was reported in 2017 that [15] Ag protrudes through the TiO<sub>2</sub> coating during the over-pressure partial melting heat treatment (OP-PMHT), even if the reason is not completely clear. It was considered that protrusion could be eliminated if most of the densification takes place before the heat treatment (pre-densification of the wire). Around the same time [16], experiments reported the presence of electrical shorts in very heavy coils, whose origin was the presence of silver bridging between adjacent turns. The last two publications appeared at the same time and it is not clear if the Ag bridges (electrical shorts) were caused mainly by the over-pressure or mainly by the weight of the coil, or by the combination. In any case, FSU opted for a combination of thin TiO<sub>2</sub> coating and mullite braiding: TiO<sub>2</sub> coating prevents the reaction between silica and silver, while the braiding guarantees a robust electrical insulation [17].

In this technical note, various commercial acrylic coatings containing  $TiO_2$  particles have been examined to understand if they are compatible with Bi-2212 wire processing. The structure of the paper is the following: first, the commercial coating are introduced (Section 2). The compatibility with Bi2212 wire has been proved by measuring the critical current (Section 2.1). Then, various coating characteristics were studied: coating thickness as a function of the deposition speed (dip coating process, Section 3.2), drying time as a function of temperature (3.4) and organic binder decomposition (3.2). A reel-to-reel system (3.4)

has been assembled and was used to coat several meters of wire.

## 2. Commercial ceramic coating

The FSU coating [14] is a slurry composed of ceramic nanopowder, organic and inorganic binders, plasticizer and solvent. The slurry is applied by dip coating and remains flexible after drying (i.e. after solvent evaporation). The coating is then covered by a thin acrylic top coat which protects the coating from abrasion during handling and winding. The organic binder is decomposed in oxygen at about 400  $^{\circ}$ C, leaving only ceramic particles weakly bonded by SiO<sub>2</sub>. The definition of "slurry" is very generic: a mixture of dense, insoluble solids suspended in a liquid. Paints are a particular type of slurry, where the solid is a pigment and the liquid is a binder, usually dispersed in a solvent. In general, a paint contains four types of ingredients:

- pigment: it can be inorganic (oxide, carbonate, sulphate,...) or organic (dye)
- binder: its function is to bind pigments to the substrate. Binders can be organic or inorganic.
- solvent: water or other organic solvent, evaporating during drying.
- optional additives, like plasticizer, deflocculant, antifoaming, dispersant, surfactant. They are usually organic.

For example, in Renaissance oil paints, the pigment is a mineral (oxide or salt), the binder is walnut or linen seed oil and the solvent is turpentine (only in late Renaissance, earlier the paint was prepared without solvent). In modern acrylic paint, the pigment is an inorganic salt or oxide and the binder is an acrylic resin dispersed in water (solvent). In particular, most of the white paints are produced with TiO<sub>2</sub> pigment, because of its extreme whiteness and opacity. The TiO<sub>2</sub> pigment world production is a few millions tons per year. In this background, it becomes evident that the coating slurry prepared by FSU in [14] can be considered as a white paint. The main difference is in the choice of binder and solvent: acrylic and water for commercial paints and PVB and xylene/ethanol for the FSU coating. We decided to investigate if a commercial paint (with TiO<sub>2</sub> as pigment) could be used to form TiO<sub>2</sub> coating on Bi-2212 wires, once the acrylic binder is decomposed.

Two commercial acrylic paint (Caran d'Ache and Talens Royal) and one acrylic ink (Talens Royal) were initially selected. The selection was based on the manufacturer's description and the availability in local shops. The essential characteristics were the presence of  ${\rm TiO_2}$  as pigment (colour index name: PW6), good adhesion to different substrates (the Ag sheath in our case), strength and good dispersion of the particles. The purity of the  ${\rm TiO_2}$  is not quantitative declared by the manufacturers, however, the pigment whiteness is very sensitive to impurities, therefore, we expect high purity in high quality, white paint. The paints and the manufacturer description (as found on the manufacturer's websites) are:

- Caran d'Ache acrylic paint "Water-based acrylic paint. Smooth and flexible, does not crack. Excellent cover on cardboard, glass, plastic, metal, wood, cement). Mixes with other materials (sand, earth, starch adhesives, etc.). The pigment is PW6 (TiO<sub>2</sub>)".
- Royal Talens, Standard Series Acrylic "100 % acrylic emulsion and high-quality pigments. A very strong and flexible paint film as a 100 % acrylate emulsion is used as binder. Excellent adhesion on canvasses and walls – or on almost any other surface that you like. Pigment PW6".
- Royal Talens, Amsterdam acrylic ink "Acrylic emulsion in water.
   Made with a high concentration of high-quality pigments. The paint film
   remains flexible and prevents cracking.). Pigment PW6".

The amount of solvent, organic and inorganic content in the acrylic paints have been estimated by measuring the weight change after drying (after > 24 h, when all the water is likely evaporated) and after organic

decomposition (in oxygen flow at 400 °C for 20 h), the values are reported in Table 1. Caran d'Ache acrylic paint has the lowest solvent content, and is therefore the most viscous, but of course its viscosity can be easily reduced by adding more water. The acrylic ink is, instead, very fluid, and after preliminary dip coating tests, it became evident that several applications would be needed to achieve a sufficient thickness of the coating. Between Talens and Caran d'Ache acrylic paint, the latter was selected, because it has the highest ceramic volume when dry; this value is marginally lower than the NHFML slurry (the values in Table 1 are extracted from [14]).

A white paint for building interiors (CIPIR, Italy) was discarded, because of the extremely high inorganic content (about 65 % in volume), that, according to the manufacturer, consists of "mineral charge". This term refers generically to salts (for example carbonates and sulphates). The large among of inorganic compounds increases the change of undesired reaction with the Bi-2212 wire; in addition, salts may damage the high pressure furnace, whose super-alloy can withstand high temperature oxidation but is not specifically selected for resistance to hot corrosion (for example from sulphates). This paint was left aside in case the others would have not worked.

High quality paint manufacturers sell also acrylic binder dispersion in water, without any pigment. The reason is that, even today, artists may want to prepare their own paint, mixing the binder with the pigment of their choice. In the same way, mixing a ceramic nanopowder water dispersion with an acrylic binder allows to easily prepare a coating, without the need of high energy ball milling, sonication or other methods to disperse the nanopowder.

Schmicke acrilyc binder (50 840), Sennelier binder and Gaestercker acrylic lac (usually used as top coat) were purchased. The following stabilised ceramic nanopowder dispersions in water have been purchased by Nanography:

- Al<sub>2</sub>O<sub>3</sub>, alpha, 28 nm, 22 wt%
- ZrO2, 40-50 nm, 22 wt%
- TiO2, anatase, 25-45 nm, 42 wt%

In a first trial, the nanopowder dispersion was mixed with Schmincke acrylic binder. The coatings were homogenous, but they had a very low viscosity. A thickener for acrylic paint (Schmincke 50.557) was added to the solution, but the results were not always fully satisfactory, since, the coating has difficulty to wet the Ag-sheathed Bi-2212 wire. For the compatibility test with Bi-2212 wire, Gaestercker acrylic Lac was used because it could be the most abrasion resistant, being sold as top coat.

## 2.1. Critical current measurements

The exact compositions of the paints and nanopowder dispersions are not disclosed by the manufacturers. Among the additives (mentioned

Table 1
Composition of FSU slurry (from [14]), commercial acrylic paints and ink examined in this work.

	FSU TiO <sub>2</sub> slurry [14]	Royal Talens acrylic paint	Caran d'Ache acrylic paint	Royal Talens acrylic ink
solvent	xylene/	water	water	water
	ethanol (78 wt%)	(46 wt%)	(34 wt%)	(84 wt%)
binder	polyvinyl butyral and	acrylic resin (eventually	acrylic resin	acrylic resin (eventually
	polysilicate	SiO <sub>2</sub> )	(eventually SiO <sub>2</sub> )	SiO <sub>2</sub> )
other	plasticizer	plasticizer, deflocculant, antifoaming, siccative, dispersant, surfactant,		
inorganic vol. (mainly TiO <sub>2</sub> ) after drying	37 %	21 %	26 %	42 %

in the previous sections), there could be substances that react with Ag at high temperature, or react with elements (for example Bi) diffusing through the Ag sheath, causing a further depletion and thus a reduction of the critical current. It is very likely that the TiO2 particles in the acrylic paint are coated with SiO2, to avoid photochemical decomposition of the acrylic resin; in fact, TiO2 nanoparticles are a very effective photocatalytic material. SiO2 at too high concentration is known to react with Ag at high temperature. During the current study, we decided to follow a very pragmatic approach and verify the chemical compatibility of the coatings in the most direct way: by measuring the critical current of coated wires. After all, this is what matters at the end: the coating can contain any chemical compound as long as the critical current is almost unaffected. The coating could reduce the critical current according to three independent mechanisms: 1) preventing oxygen diffusing back to the ceramic and thus insufficient doping 2) chemical reaction with elements diffusing from the ceramic filaments 3) reaction with the Ag sheathed leading to leakages of the ceramic.

Various acrylic paints and combinations of paint or acrylic binder with ceramic dispersions were investigated and are listed in Table 2. The amount of solvent (water or ceramic dispersion) was selected to have a high viscosity, so that a thick layer of coating can be deposited in one pass. In the case of low viscosity combinations, three layers were applied. The Nanografi  ${\rm TiO}_2$  water dispersion was mixed with acrylic water dispersion (Gerstaecker Lac) and a thickener (Gaestercker 50.557).

A Bi-2212 Ag sheathed wire (PMM200205-2) was purchased from Bruker Energy and Supercon. Technologies (Bruker EST) in the USA. Several pieces of about 2 m long were cut from the spool. On each piece, one or more sections (20-50 cm long) are coated, while one section (30–50 cm long) is left without any coating; this uncoated section would provide the reference I<sub>c</sub> value for that particular wire piece. The 2 m long wire piece is wound on a cylindrical steel support of 40 mm in diameter and 50 mm in height (the so-called barrel). After the organic decomposition and the OP-PMHT, copper rings are attached to the cylinder with screws, the wire ends are soldered to copper terminals and voltage tap pairs are soldered to the wire on each section. The barrel is then mounted on the probe for I<sub>c</sub> test. The barrels and their different sections are summarized in Table 3. The critical currents were measured at 4.2 K, 10 T or 15 T, the  $I_c$  criterion was 0.1  $\mu$ V/cm. As shown in Table 3, the  $I_c$ values measured on the coated sections differ by less than 3 % from the non-coated values in all cases: this demonstrate that the water-based acrylic paints and the ceramic dispersions are compatible with Agsheathed Bi-2212 wire processing. In general, the I<sub>c</sub> variation over several meters of wire can exceed 10 %; therefore, the variation of less than 3 % observed in coated sections can be attributed to the intrinsic variability along the length, rather than to the effect of the coating process. Among the coating formulations in Table 2, Caran d'Ache diluted (1:0.35) with TiO2 dispersion was selected for additional characterisation. The reason is that the use of TiO2 dispersion instead of water would provide a slightly higher ceramic content in the dried coating (32 % instead of 27 % in volume). The 1: 0.35 dilution factor should provide a relatively thick coating (20 to 50 µm, depending on the coating speed, see Section 3.3 for more details).

Table 2

List of acrylic paints and combinations of paint or acrylic binder with ceramic dispersions studied in this work.

Caran d'Ache acrylic paint + water (1:0.6); three layers

Talens Acrylic Ink; three layers

Nanografi  ${
m TiO_2}$  water dispertion + Gerstaecker Lac (acrylic binder), thickener 50557; one layer

Caran d'Ache acrylic paint + nanografi  $TiO_2$  dispersion (1:0.8); one layer Caran d'Ache acrylic paint + nanografi  $Al_2O_3$  dispersion (1:0.6); one layer

**Table 3**Summary results of barrels coated with acrylic commercial paints and water dispersions. The percentage variation is calculated with respect to the noncoated value.

barrel		coating	$I_c(A)$
#1	Section	none	886 A at 10 T
	1		
	Section	#2 Talens Acrylic Ink	864 A at 10 T
	2		-2.5 %
#2	Section	none	657 A at 15 T
	1		
	Section	#1 Caran d'Ache acrylic paint + water	648 A at 15 T
	2	• •	-1.4 %
#3	Section	none	810 A at 10 T
	1		
	Section	#5 Caran d'Ache acrylic paint + Al <sub>2</sub> O <sub>3</sub>	832 A at 10 T +
	2	dispersion	2.7 %
	Section	#3 TiO <sub>2</sub> water dispersion + Gerstaecker	820 A at 10 T +
	3	Lac, thickener	1.2 %
	Section	#4 Caran d'Ache acrylic paint + TiO <sub>2</sub>	809 A at 10 T
	4	dispersion	-0.1 %
		1	

## 3. Acrylic coating characteristics

With the aim of applying a thin, homogeneous coating over long wires, it is necessary to study some of the coating characteristics: agglomerates and particle size for different compositions (Section 3.1), coating thickness versus withdrawn speed (3.3), the decomposition of the organic binder (3.2) and drying time. Finally, the reel-to-reel system is described in 3.4.

Regarding the mechanical characteristics of the acrylic paint, the coating is very flexible, and the coated wire can be bent on 5 mm radius without damage. After decomposition of the organic binder, the ceramic particles are weakly bonded to each other and to the Ag sheath: the coating can be scratched with a metallic blade but do not leave marks on fingers.

## 3.1. TiO2 particle size

The size of  $TiO_2$  particles and/or agglomerates should stay within a certain range, in order to be used as insulating coating on Bi-2212 wire. In fact, too fine powder may lead to insufficient porosity and the oxygen diffusion could be reduced; too coarse powder, say several tens of

micron, would make it difficult to prepare thin coating (less than 50  $\mu m$ ). A laser particle size analyser (Horiba Partica LA-950 V2) was used to measure the particle size distribution. The Nanographi TiO2 dispersion (see Fig. 1) contains mainly particles below 100 nm. Instead, the Caran d'Ache acrylic paint contains coarse particles, up to a few microns. The mixture of Caran d'Ache acrylic paint with Nanografi TiO2 water dispersion (ratio 1:0.35 in weight) has a peak at around hundreds of nanometers, as observed in Caran d'Ache paint alone; the peak at less than 100 nm is absent, but a tail extends to over 10  $\mu m$ , which is probably due to aggregates formed from the interaction with the TiO2 water dispersion. Later, when this composition was used for coating long length wire on the reel-to-reel system, it was observed that little agglomerates are present in the coating, say few times every meter of wire. It could be better to use pure water instead of the TiO2 dispersion to dilute the acrylic paint.

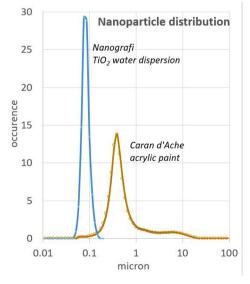
The  $TiO_2$  coating prepared by FSU has a negligible change in thickness after organic decomposition [14]. It follows that the ceramic coating (after binder decomposition) has a very low density and is very porous, only about 25 % to 40 % of the volume being occupied by inorganic material (mostly  $TiO_2$ ). This is of course a positive feature, because the coating should allow the oxygen to diffuse easily. We have not observed any significant change in thickness (after acrylic binder decomposition) in the coating prepared with Caran d'Ache acrylic paint.

After partial melting heat treatment (PMHT), all the coatings shows a fine crystalline structure (few hundreds of micron) and a yellowish colour (see Fig. 2), perhaps due to the contamination by Bi which is diffusing through the Ag sheath. Also the coating prepared by FSU (see for example Fig. 5 in [14) has a yellow/green colour.

## 3.2. Organic binder decomposition

The organic binder, and eventually any other organic compound that could still be present in the dried acrylic paint, could be decomposed before the OP-PMHT. The decomposition can be carried out in a reducing atmosphere (air or oxygen, the so-called oxidative pyrolysis) or in inert atmosphere (for example He, pyrolysis).

A sample of Caran d'Ache acrylic paint diluted with Nanografi  $\text{TiO}_2$  dispersion (1:0.35) was placed in a thermogravimetric analysis system (Mettler Toledo Star System TGA/DSC 1). The weight loss is shown as a function of temperature in Fig. 3; the temperature ramp was 5 K/min. When the acrylic paint is heated in He gas (pyrolysis), the final mass loss is almost the same as in oxygen, however, the remaining ceramic sample



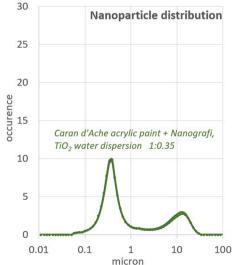


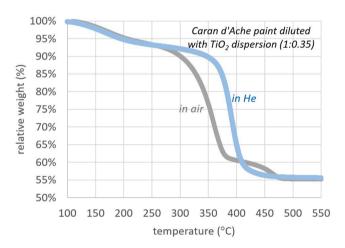
Fig. 1. Left: particle size distribution in Nanografi TiO<sub>2</sub> dispersion and Caran d'Ache acrylic paint. Right: particle size distribution in a solution of Nanografi TiO<sub>2</sub> dispersion and Caran d'Ache acrylic paint (ratio 1:0.35).

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# Caran d'Ache Nanographi TiO<sub>2</sub> dispersion

**Fig. 2.** Photograph of coated wire after organic binder decomposition and over-pressure partial melting heat treatment. Left: Caran d'Ache acrylic paint + nanografi  $TiO_2$  dispersion. Right: Nanografi  $TiO_2$  water dispersion + Gerstaecker Lac (acrylic binder).

→ 100 micron



**Fig. 3.** Thermogravimetric analysis of the coating prepared with Caran d'Ache and Nanografi TiO<sub>2</sub> dispersion (1:0.35); the temperature ramps was 5 K/min.

looks light grey in colour, indicating that small amount of organic material (for example amorphous carbon) is probably still present in the ceramic. The decomposition in inert atmosphere does not provide any advantage, because all the materials in a coil can withstand the OP-PMHT heat treatment at 890 °C in 1 bar oxygen, therefore, the decomposition process was carried out in oxygen (for example for the barrels in Section 2.1). In this case (oxidative pyrolysis), the evolve gas analysis during TGA experiments (EGA-TGA) in air was performed and, as expected, the decomposition products were  $\rm CO_2$ ,  $\rm CO$  and water. Trace of S compounds were also detected, probably due to surfactants decomposition. Therefore, no residues should be present on the wire surface.

The TGA has been used to create a heat treatment schedule for the oxidative decomposition of the organic binder. It is clear that the temperature ramp should be decreased between 300 °C and 350 °C because a too violent decomposition reaction may lead to detachment of the coating. We expect some very weak bonding between ceramic particles after the organic decomposition, because it was reported that necking (the first stage of sintering) takes place already at 500 °C for TiO $_2$  prepared for photocatalytic applications. Indeed, after decomposition of the

organic binder, the ceramic particles are weakly bonded to each other and can be removed by scratching with a metal blade. As in the case of the FSU coating [14], the ceramic particles provide insulation by acting as spacers between winding turns. The impregnation will immobilize the ceramic particles.

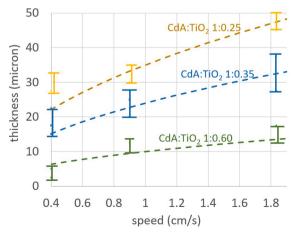
## 3.3. Coating thickness

In general, dip coating processes can be used to deposit coating with thickness up to 100  $\mu m$ . In the dip coating process, the thickness of the coating is the combined result of viscous force, gravity, surface tension and inertial force. For relatively high speed (cm/s) and viscosity (the so-called viscous flow regime), only gravity, speed and viscosity enter in the equation: the thickness, d, is  $d \propto \sqrt{\frac{\eta U}{\rho g}}$ , where  $\eta$  is the viscosity,  $\rho$  the density and U the speed.

The thickness of the coating was measured on short pieces of wire (5 cm) at different extraction speeds. Three different compositions with increasing viscosity were prepared, diluting the acrylic paint with  $\rm TiO_2$  water dispersion at 1:0.60, 1:0.35 and 1:0.25 in weight; the withdrawn speeds were 0.4 cm/s, 0.9 cm/s and 1.8 cm/s, covering the whole range which could be applied with the system in the laboratory. This speed range is also suitable for long length, reel-to-reel coating. The measured thicknesses are plotted in Fig. 4. Three or four samples were tested for each combination of speed and composition and the error bars in Fig. 4 are simply the variability among similar samples. The measured thicknesses are more or less linear when plotted as a function of the speed square root. These results indicate that a combination of viscous solution and high speed should be selected to obtain a thick coating in a single application.

## 3.4. Reel-to-reel coating

It takes at least 15 min for drying the diluted Caran d'Ache acrylic paint at room temperature. The coating is considered "dry" when it is does not stick when touched; it is the so-called "tack free" and should correspond to a complete (or almost complete) evaporation of water. It is evident that this time is too long for a reel-to-reel application, then the drying time must be shortened by increasing the temperature. The drying time was measured at different temperatures (see Fig. 5) on short pieces of wire. At about 150–170 °C, the time is less than a minute; this time corresponds to a distance of the order of a meter for a speed of about 1 cm/s. The high temperature should not have a detrimental effect on the acrylic resin because the DTA has shown that there is negligible weight variation up to at least 200 °C (see Fig. 3).



**Fig. 4.** Thickness of the coating as a function of the extraction speed for three different composition (1:0.25, 1:0.35, 1:0.6) of the coating prepared with acrylic paint and  $\text{TiO}_2$  dispersion. Dashed lines are guide for the eye.

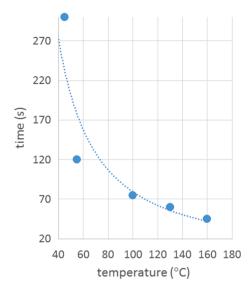


Fig. 5. Drying time versus temperature for a thin coating (20–30  $\mu$ m) of Caran d'Ache paint diluted in water (1:0.35). The line is a guide for the eye.

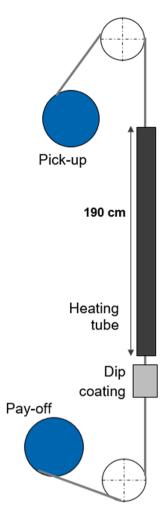
A reel-to-reel system was assembled including a 1.8 m long heating pipe. The situation in the heating pipe is actually more complex than the short piece test. In fact, in the heating pipe cold air enters from the bottom aperture and is heated up while moving upward. The temperature gradient along the pipe was confirmed using a thermocouple. After several tests, the speed was set at about 0.85–0.95 m/s, resulting in a coating thickness of about 25–30  $\mu m$ .

A sketch of the reel-to-reel coating line is reported in Fig. 6. A clutch on the pay-off spool provides some tension (about 1 kg) to the wire. The wire passes around a pulley and enters the dip coating unit. Most of the dip coating reel-to-reel systems use a wheel to guide the wire into the coating bath. Instead, in our system, the wire passes through a seal and enters the (small) coating bath from the bottom. We find that this system needs less liquid and is easier to clean after the use than conventional systems. After dip coating, the wire enters the heating pipe. At the top, a pulley guides the wire to the pick-up spool, which is driven by a motor. The longest wire coated so far was about 20 m. Part of the wire (9 m) was used to wound a small coil, and its critical current was in line with expectations, confirm that the acrylic paint has, so far, no detrimental effect on the critical current.

## 4. Application to coated conductors

It has been shown [18] that  ${\rm TiO_2}$  coating has a relatively high thermal conductivity at low temperature, when compared with other ceramics and of course with plastics. High thermal conductivity is beneficial for quench protection, because it favours the enlargement of the current sharing region [19], by spreading the heat over a larger volume; of course, at the same time, an additional benefit is the reduction of the hot spot (peak) temperature. The formulation of the coating used in [18–19] was not disclosed, but it is reasonable to think that the  ${\rm TiO_2}$  formed with commercial paints can also provide enhanced thermal conductivity.

Caran d'Ache declares that the paint has good adhesion to various materials, including metal and plastic. The paint was applied to coated conductor tapes by dip coating and, of course, the organic binder was not decomposed. The thin coating is flexible and does not crack even when the coated tape has been bent in liquid nitrogen, in contrast with what happen with many other plastics, which breaks simply when cooled to 77 K, even without applying any deformation. Probably, the presence of TiO<sub>2</sub> particles reduces the thermal contraction of the acrylic/TiO<sub>2</sub> composite to a sufficiently low level, and the thermal strain resulting from the differential thermal contraction between the REBCO



**Fig. 6.** Sketch of the reel to reel system assembled in this work. The wire on the bottom spool passes through a dip coating system, then enters the heating pipe (black, temperature as high as 180  $^{\circ}$ C), where the coating dries. The wire is then wound on a pick-up spool attached to a motor.

tape (Hastelloy is the dominating material) and the acrylic resin is below the ultimate strain for the resin. Therefore, the acrylic white paints could be then used also as an insulating material for coated conductors, with additional high thermal conductivity when compared to polyimide-imide coating.

## 5. Conclusions

White commercial acrylic paints containing  ${\rm TiO_2}$  nanoparticles as pigment have been investigated for preparing ceramic coating on Agsheathed Bi-2212 wires. The chemical compatibility with Bi-2212 wire processing (winding and overpressure heat treatment) has been proved by measuring the critical current of coated and non-coated wires, and it was found that the difference in I $_{\rm c}$  (4.2 K, 10 or 15 T background field) is less than 3%. A reel-to-reel system was assembled and tens of meters of Ag-sheathed Bi-2212 were coated. Coating thickness can be adjusted between 10 and at least 50  $\mu m$  (in one pass) by varying the viscosity of the solution and the withdrawn speed. Wire lengths up to 20 m have been coated so far.

In [16], FSU proposed to increase the thickness of the ceramic coating (up to  $37~\mu m$  was tested in [16]) as a possible solution to the electrical shortcuts caused by Ag protrusion across the coating. The acrylic-based coating described in this technical note has reached a thickness almost twice than the one in [16], potentially eliminating the risk of electrical shorts. Of course, large thickness could be achieved also

with the FSU coating described in [14], adjusting the viscosity and the withdrawn speed.

In general, the preparation of  ${\rm TiO_2}$  coatings from raw materials requires specialised equipment (like glove boxes, sonication or ball milling) which are not always available in applied superconductivity laboratories. This technical note suggests that commercial acrylic white paints are a rather simple and straightforward approach to deposit  ${\rm TiO_2}$  ceramic coatings on Bi-2212 wires.

## CRediT authorship contribution statement

**D. Uglietti:** Conceptualization, Investigation, Writing – original draft. **A. Testino:** Investigation, Writing – review & editing. **R. Sobota:** Investigation, Writing – review & editing. **D. Nardelli:** Investigation, Writing – review & editing.

## **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Data availability

No data was used for the research described in the article.

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