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PROPERTIES OF FILLERS IN PUTTIES BASED ON ACRYLOID B-72

Julie Wolfe and Talitha O'Connor

Abstract

Bulking Acryloid B-72 with fillers to make putties can have great flexibility due to the enormous range of products available for this application. Individual characteristics of each filler type will modify the properties of the polymer in different ways. This paper presents an initial phase of research designed to study the effects of fillers in B-72, to understand the difference between bulking with carbonates, silicates, sulfates, or organic compounds. In this phase, the fillers and resin were chosen to represent a set of putties that could be used for loss compensation on white marble in an indoor setting. A systematic study has been limited to one resin mixture, 60% B-72 w/v in acetone, isolating a group of 21 different fillers. Sample coupons of the dried putties were tested to compare color, gloss, reflectance, and Vickers hardness. Compiling this data into a reference chart is ongoing. With continued study, the results should allow for improved comparison of their properties, enabling the conservator to choose the most appropriate mixture for specific treatments.

Introduction

The long-term goal of the topic presented in this paper is to design a comprehensive palette of fill mixtures that can be used on indoor marble sculptures. The aim is to better understand the individual properties of fillers to allow conservators to approach filling more like inpainting. Ideally, fills that mimic the marble would eliminate the need for inpainting. Technical studies can additionally categorize fillers according to their mechanical and physical properties as they modify B-72. Classifying putties with specific filler types for their color, strength and workability could lead towards a practical database for distinguishing one or more fillers for a specific application.

The challenge in creating putties for loss compensation in marble is due to the fact that no two pieces of stone are exactly alike. White marbles are composed of dolomite and calcite with a wide variety of minerals affecting its color, texture and characteristic particle morphology affecting its translucency (Solomon and Hawthorne 1983). Since conservators work with marbles of such subtle variances, no one single recipe could suffice. Having a fill that mimics the appearance of marble is not the only desirable property. Adopting the list from John Griswold and Sari Uricheck (1998), the putty should also be workable, carvable, stable, reversible, non-shrinking, lacking air bubbles, and variable in hardness, color and translucency.

With the variety of fillers available, comparing their properties is a complicated technical study to control. As explained by Plueddmann and Stark (1977, 1), "the interface between polymer and filler involves a complex interplay of physical and chemical factors related to composite performance". Keeping in mind the interfacial relationship between the filler and resin polymer, resin modifications based on solvent type and specific properties of the filler allow for an unlimited number of variables. Filler properties such as particle shape, particle size, and refractive index may modify the composite in hardness, translucency, color, slump and more. Within the conservation literature, there have been several studies on fillers in resins that have either focused on a limited number of fillers, or one mixture (Gänsicke and Hirx 1997; Nagy 1998; Griswold and Uricheck 1998; Larkin and Makidrou 1999). With these studies in mind, the authors hope to expand on their work with the aim of perfecting the putties for specific applications.

Strategy for the study

The strategy in this study acknowledges the complexity of this topic and assumes the need to plan a series of phases that will systematically isolate the properties of each composite. This first phase attempts to reduce as many variables as possible by isolating one filler type, in one resin system, and one solvent. B-72 and acetone were chosen as the resin-solvent mixture. This is a common resin-solvent system currently used by conservators, the quick evaporation of acetone may prevent slumping in comparison to other solvents, and the authors have found that in use, acetone allows the putty to set up in reasonable working time. Putties were prepared and cast into sample coupons that could be used for testing as described throughout this paper. All were mixed in B-72 at 60% w/v in acetone. Each filler in turn was added to 30 ml of the resin-solvent mixture and the putty cast into three round coupons, 2 cm diameter and approximately 1/4" thick. These coupons were used to test hardness, color, gloss, and reflectance.

Variables were difficult to eliminate when preparing the samples, and as the goal was to test putties under real-life conditions it was impractical to follow industrial standards. Each recipe required different filler-resin concentrations to obtain workable putties. For example, fumed silica can be added to approximately 200% of the weight of B-72 before breaking apart, whereas a crushed marble can only be added to approximately half that quantity. The acetone solvent created another unavoidable variable in viscosities. During sample preparation, it was inevitable that the acetone would evaporate at different rates and cause the putties to have slightly different working properties. The viscosity of each putty was not measured during this phase, and the workability among them varied in texture and quality. Variables were minimized by having a structured routine for the sample preparation and one person preparing the coupons.

Choosing a resin concentration

As Larkin and Makidrou found in 1999, different fillers require very different filler-resin ratios to give the best results. In order to determine one resin concentration for the study, it was necessary to test each filler in a range of concentrations and select one that would accommodate all of the fillers. Starting with 20%w/v and working up in 10% increments, we found that all of the fillers were best used in a resin concentration of 60% w/v. Having only tried between 20-60% w/v concentrations, we cannot generalize that this is the best concentration, however this small study did show the 60% as having the greatest range of workable putties at different filler concentrations and produced fewer samples that broke apart or cracked when dry. The concentration study also helped to reduce the filler list from thirty to twenty-one, as it identified ones that were difficult to work with or could have complicated the study. Eliminated fillers are listed in Table 3 (all tables appear after the text).

Choosing a filler concentration – the final recipes

The concentration for each filler varied since their capacities to bulk were different. As the resin concentration tests were being carried out, the authors determined the threshold limit for adding fillers to 60% w/v B-72. The filler was added in ¼ teaspoon increments to 30 ml of B-72 and a small sample was taken each addition of more filler. The procedure continued until a stiff putty could be worked without breaking apart as seen in Figure 1. During this process, the working properties of the wet putties were noted and can be found in Table 2 under the putty observation column. The putty was described as gritty, spongy, gummy or stiff/taffy. Wet putty texture is expressed by the authors as "gritty" if it felt like wet sand, "spongy" if it felt airy and had some spring like frosting, "gummy" if it felt like chewing gum and a little sticky, and "stiff/taffy" if it was dense and hard to compress like a soft caramel candy.

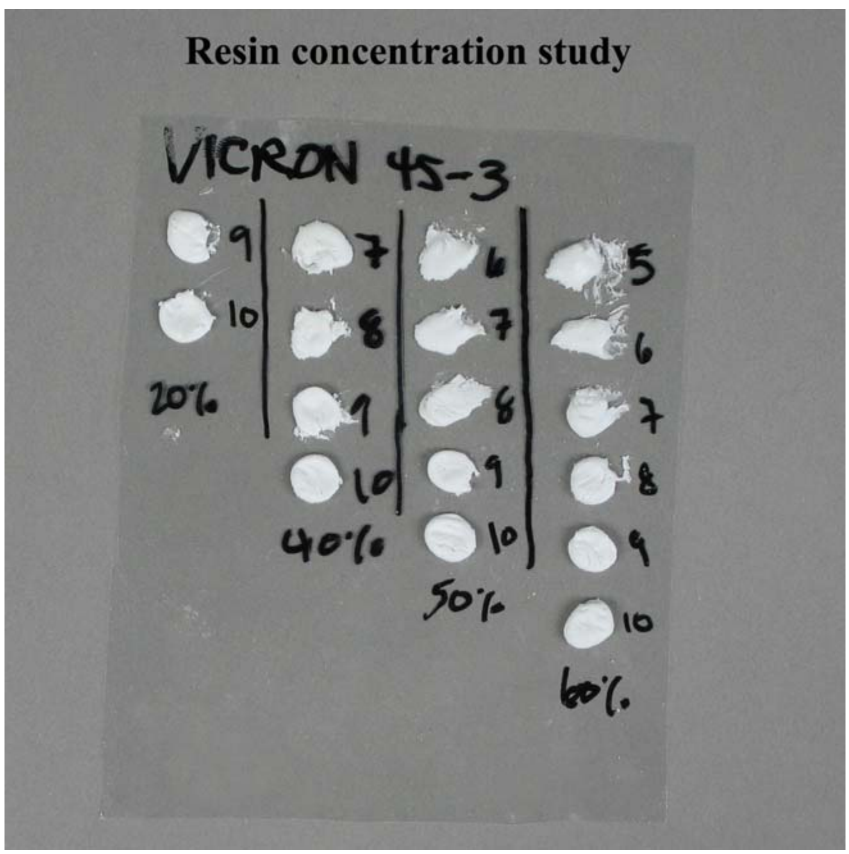

Figure 1. Testing the fillers at different concentrations.

The final recipes for the putties in this study are given in Table 1. The chosen recipe contained a filler to resin concentration that was ¼ teaspoon below the identified threshold limit. The filler was mixed in 30 ml of 60% w/v B-72 in acetone and cast into three polycarbonate cups lightly coated with Vaseline petroleum jelly. For one of the three coupons, the bubbles that formed on the surface were filled using a spatula with a putty made from the same recipe. One set with a flat, even surface was required for the optical testing. Sanding the face of the filled coupons was done on rotating sanding wheels with Buehler sanding paper and micromesh to 12,000 grit. The face of the polished coupon was taped across one half and sandblasted to give a sample having the maximum obtainable gloss in addition to a matte surface. The final set of test coupons grouped by filler class is illustrated in Figure 2.

Figure 2. Final set of test coupons, grouped by class.

The only filler that had a slightly different preparation method was the Aerosil R-7200. An additional step was required to obtain a workable putty. Fumed silicas are difficult to use in acetone, and Degussa (2005) recommends using a product that is treated with a methacryloxy functional silane. The putty bulked with the R-7200 crumbled after drying as seen in Figure 3. This crumbled sample was ground in a coffee grinder to make a filler comprising both the resin and fumed silica. This ground up powder was then added to the regular 60% w/v B-72 mixture resulting in a stronger composite that did not break apart (Figure 4). While testing different fumed silicas, it became apparent that by using this two-step process, crushing the first bulked resin and adding it to more resin, it is possible to get more filler into the system without it fracturing. The authors feel that more testing needs to be done on fumed silica for this resin-solvent system in the future.

12.5 teaspoons Aerosil R-7200 mixed with 30 mL 60% w/v B-72 in acetone.

Figure 3. Putty bulked with Aerosil R-7200, showing crumbling after drying.

Two Phases:
12.5 teaspoons Aerosil R-7200 mixed with 30 mL 60% w/v B-72 in acetone. Dry putty crushed. Added to 30 mL B-72 in acetone with an additional 12.5 t. R-7200.

Figure 4. Putty shown in Fig. 3, after reconstitution using two-step process.

Since four of the fillers in this study are listed as California Prop 65 carcinogens, the Getty's safety officer, Scott Fife, monitored the air during sanding. The potentially carcinogenic fillers include ATF 40, cristobalite, talc, and VICRON 45-3 according to their MSDSs. Fife found that with the aid of a portable Nederman air extraction unit having a particulate filter, the dust levels were kept below the permissible limit of exposure. Any silicaceous particle below 10 micron can travel to the alveoli of the lungs. The air was sampled using a Gilair 3 sampling pump set at 2.5 liters per minute, with a 37 mm, 5 micron PVC filter with an SKC aluminum cyclone attached. Analysis method was NIOSH 600 – Gravimetric and NIOSH 7500 – X-Ray Diffraction Spectroscopy for silica analysis. Broadspire/NATLSCO Risk and Safety Services conducted the analysis. The results for the permissible limit of exposure were concluded based on the specific sanding procedure carried out for this study.

About the fillers

The final set of fillers includes a range of carbonates, silicates, sulfates, and cellulose powder. . The number of fillers tested was narrowed down to twenty-one, and are listed in Table 1 along with the recipe for the putty in a 60% w/v B-72 mixture. The collected properties for each filler and conclusions about the putty properties are listed in Table 2. The final set was chosen to include a range of types, fillers that are typically being used in the field of conservation, and ones with minimal processing and surface coating. At this time, not all of the properties of the dry fillers themselves have been determined, but eventually the properties will be added to Table 2 as the study progresses. Microscopy will be used to determine the particle shapes and refractive indices. X-ray diffraction was used by Giacomo Chiari, scientist at the Getty Conservation Institute, to confirm the composition of the purchased alabaster and Thassos marble samples.

John Larson published the use of crushed and boiled alabaster for marble filling, and it is a common choice among conservators (1978). The change in properties that occurs as a result of boiling is not exactly clear; however, it has been noted to change its hardness and translucency (Pullen 2004). Alabaster for this study was purchased from a local marble supplier and Giacomo Chiari used x-ray diffraction to confirm the composition as calcium sulfate. Pieces of the alabaster were boiled in water at 97 degrees Celsius for three hours. The alabaster then showed greater opacity and became notably softer to crush (Figure 5). Both boiled and unboiled alabaster was hand ground for comparison in the study, and even though there were slight differences in the properties of the dried putties, it was not significant enough to warrant making a major distinction. The boiled alabaster appeared to produce less overall surface gloss, a slight shift in color to a more yellow tone, and a slight increase in brightness. The hardness of the dried putty remained about the same.

A white marble from Thassos was purchased from a local supplier for hand grinding, and the stone was identified as calcium and magnesium carbonate using x-ray diffraction. Stephan Simon at GCI suggested baking the Thassos to modify its properties. Studies made by Malaga-Starzec indicate that "intergranular decohesion begins at temperatures between 40-50ºC (104-122ºF) for some marble types" due to thermal expansion and contractions – calcite more than

Figure 5. Test using crushed and boiled alabaster.

dolomite (Malaga-Starzec 2003, 306). The Thassos marble was baked for 12 hrs at 600 ˚C (1112ºF) to force micro fracturing between the grains and increase its porosity (Figure 6). The measurements of surface hardness using Vickers showed that the baked marble became softer than the unbaked stone by a factor of two, making it noticeably easier to crush. In contrast, a dry coupon made with the baked Thassos appeared to be harder than the sample coupon with unbaked Thassos. This implies that baking (at least in the case of this marble) causes the marble itself to be softer, but not necessarily the dry putty. The baked Thassos stone became more opaque, and more yellow in tone, and this change in color and opacity was similarly reflected in its properties as a dried putty.

The hand crushed Thassos was sifted into six different groups having particle sizes between 0.075mm and 0.6mm to determine any measurable differences between them as bulking agents. The authors predicted that smaller particle sizes would generally give dried putties having higher gloss potential, harder, and an increased brightness. Unfortunately, the small study did not show any obvious pattern in property changes; the effect of particle size in bulking will require a more focused study in the future. All of the Thassos coupons gave similar fill results. All had a bluish tone, mottled surface, similar hardness, and fairly low gloss potential.

Figure 6. Test using baked Thassos marble.

Visual Observations

The coupons were examined visually using the unaided eye before technical analyses to note shrinkage, surface appearance, surface bubbles, sandability, and carvability. Shrinkage is an important factor in workability, and a high shrinkage could cause compressive strain on the object being filled. The casting molds had a diameter of 2 cm, so the coupons were simply measured after they dried completely. Shrinkage was not an obvious problem with this set of putty mixtures, with the exception of Aerosil R-7200, which showed the greatest change. A small amount of shrinkage was noticed in the coupons with talc, calcite, Marbledust-M, and the sulfates. Cracking of the dried putty matrix can indicate a poor relationship between the resin-filler-solvent system. Cracking was found to be more common with the sulfate class, such as alabaster plaster, and terra alba. The carbonate Vicron 45-3 dried with a single crack across the middle. The coupons with blanc fixe and precipitated calcium carbonate dried with a wrinkled surface that seemed to be caused by the surface drying much faster than the center of the putty. A difference in homogeneity was noticed, as some of the putties dried with a mottled surface coloring, indicating flocculation of the particles. Mottled surfaces included the alabaster plaster, glass flakes, talc, Marblewhite 200, and ViCALity Ultra Heavy. The creation of bubbles was a problem with nearly all of the fillers. Fast evaporation of the solvent at the surface of the putty inherently traps air bubbles. The three fillers showing the fewest bubbles respectively include the ViCALity Ultra Heavy, Vicron 45-3, and glass flakes. Two of the fillers, K15 Scotchlite and cellulose powder, were difficult to sand because they were so soft, and seemed to collect dirt and darken in the process.

Hardness

A fill that is softer than the stone being repaired is one desirable characteristic. A Buehler Hardness testing instrument measuring Vickers (HV) was used at the Dental School of the University of California in Los Angeles. The instrument creates a 136º pyramidal mark with a diamond-tipped indenter onto the surface of the sample. The indentations were made at a range between 25-500 gram force (gf). The length of each diagonal line of the mark was measured using a graticle and a 40X oculus. Five measurements were taken across the face of each sample. The instrument calculates the HV dividing the force by the surface area of the indentation. Each coupon had a slightly different resistance to indentation and required different force settings. For example, the harder samples required higher force. Unfortunately, since all the coupons required micro forces below 500g, care must be taken when comparing HV results that were taken at different force ranges. Another complicating factor is the variation in hardness found across the surface of single coupons. It is most probable, that the range in particle sizes for some of the fillers causes the variation, therefore, the hardness of some putties can be rather inhomogeneous on a micro scale. At this time, a general summary of the result can be presented, however no overall data will be reported to prevent possible misinterpretation. In reality, conservators would not know the actual HV of the art material that requires filling, but this method should allow general categorization of the putties as hard, medium or soft by averaging the five HV results for each coupon. The fillers have been generally ranked in Table 4; however, the chart should only be considered a rough idea of the difference in hardness between the coupons.

One positive characteristic noted from comparing the putties and actual marble, is that most of the fillers produced putties that appear softer than the marble. Most of the fillers increased the hardness of 60% w/v B-72 in acetone, with the K15 glass microballoons, Aerosil R-7200, talc, cristobalite, blanc fixe, and precipitated calcium carbonate being probable exceptions. One aspect of the overall study that has not been carried out, includes drying times for all of the different putties. There is some concern by the authors, that even though all of the sample coupons were dried for one month, some of the fillers might prolong drying time, and give an abnormally low HV reading. This is another example of why the HV results cannot be fully interpreted at this time.

The fillers with larger particle sizes and wide particle size distribution show a greater range of HV across the surface. Comparatively, a sample of actual Thassos marble also shows a range of hardness across the surface. The surface hardness of the pure Thassos was compared with the baked Thassos sample and showed a reduction in hardness by an approximate factor of two after baking. In contrast, this was not necessarily true between the two putty coupons, as the pure and baked Thassos fillers gave similar hardness values to the dried putties. The boiled and unboiled pure alabaster samples also showed a reduced hardness by an approximate factor of two after boiling. As with the marble, the pure and unboiled alabaster when used as a filler did not show any significant difference in hardness.

On a side note, no correlation was seen between the HV results and the actual carvability of the dried putty. Some of the fills were quite difficult to carve, including: all crushed Thassos, ATF 40, calcite, Marbledust-M, precipitated calcium carbonate, and cristobalite. Of these hard-to-carve putties, their HV values are random and ranged from HV2 to HV70. Though possessing a lower HV than actual marble, it appears that these values cannot be associated with practical information on carvability. None of the current test results have allowed reference for fillers giving putties that can be safely carved around a marble surface. Carvability is a characteristic that requires future attention.

Optical Properties

One of the greatest challenges in matching a bulked resin to marble is that their optical properties are so inherently different. They reflect, transmit, refract, disperse and polarize light to varying degrees, making the analysis of these properties extremely complex. Preliminary work includes taking measurements of gloss, percent reflectance, and color. The results obtained thus far are encouraging, however a discrepancy between measured reflectance values and visual comparison indicate that more work needs to be done.

Gloss

Gloss measurements were taken using a Nova-Color gloss meter borrowed from the Detroit Institute of Art's Conservation Department. The meter is capable of measuring surface reflectance at 20, 60, or 85 degrees. The measurements were given in gloss units (GU) where 100 is all specular light, as you would find in a perfect mirror. Low gloss units indicate diffuse reflection as on a matte surface. The meter was calibrated using a standard before measuring the coupons. All samples were polished to 12,000 grit. Three measurements were taken from each coupon, rotating it 90º for each reading at 20, 60, and 85 degrees. Rotating the sample was done in case there was a difference in gloss based on the direction of sanding, or small scratches. After averaging the results for each set of three measurements and ranking the fill coupons from matte to glossy, a slight difference in the order was noted at each reflectance angle. Table 4 ranks the GU from high to low for all of the samples at 60 degrees. (The ranking at this degree was comparable to the authors visual rankings in gloss using an unaided eye.)

Figure 7 shows the coupon set in a strong raking light to show the variation in surface gloss. In general, the carbonates and sulfates with small particle sizes obtained the most gloss—even higher than the polished pure Thassos marble. In contrast, fillers with larger particle sizes and wider particle size distributions such as the crushed Thassos and ATF 40 were at the lower end of the gloss scale and could not achieve as much polish as the pure Thassos. The sulfate class had a wide gloss range, whereby the blanc fixe obtained the highest polish and ground alabaster the lowest. The silicate group also had a wide gloss range with the K15 microballoons having the lowest polish of all the tested fillers, and the Aerosil R7200 being the silicate with highest polish.

The comparison of gloss units between the high polished coupons and actual marble can give us greater judgment in choosing an appropriate filler for putty-making. For example, as the hand ground Thassos coupons gave gloss units well below that of the pure Thassos sample, they might not be a good choice for the compensation of highly polished marble (at least, if used alone). Fillers with larger particle sizes and wider distribution also tended to obtain lower levels of gloss.

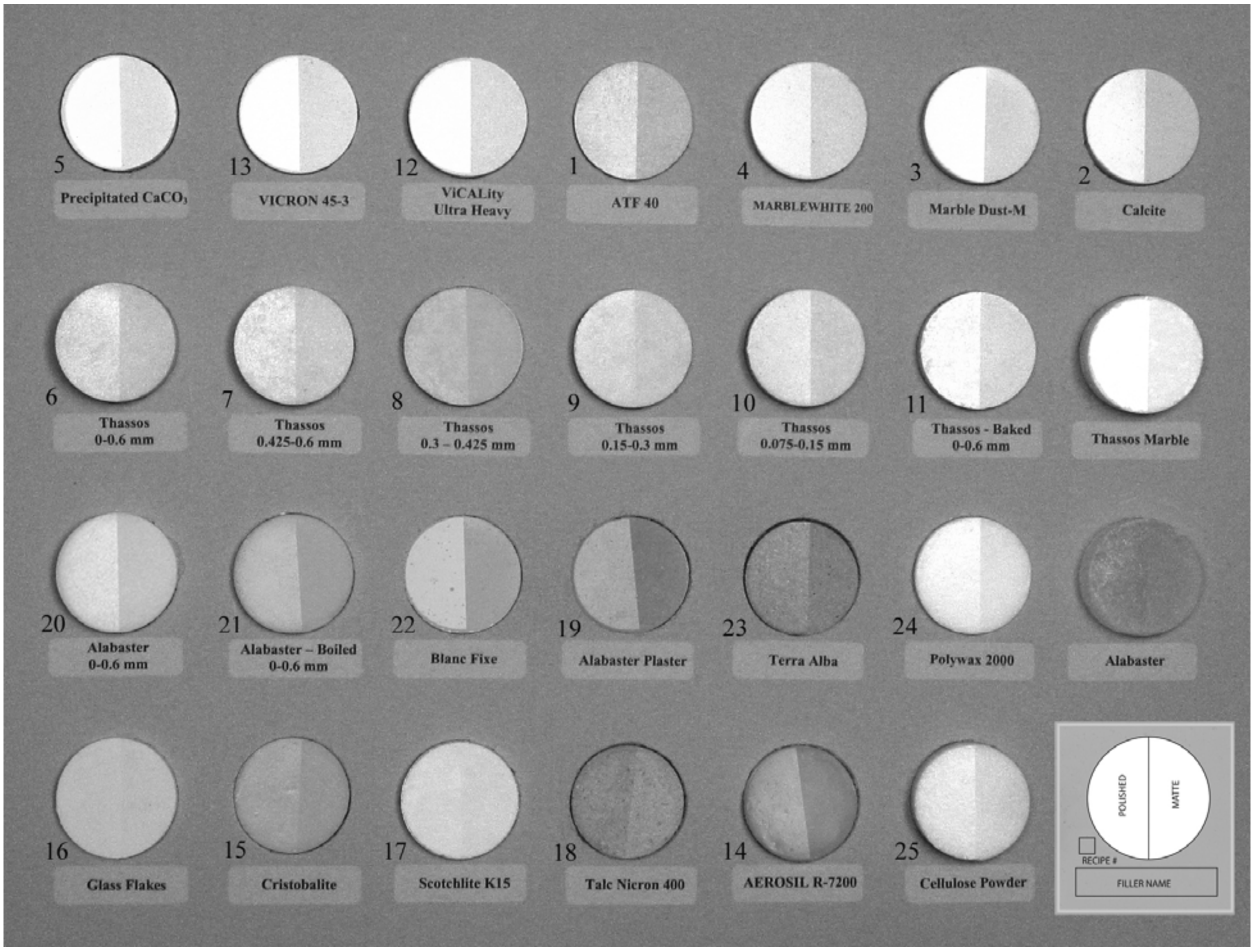

Figure 7. Coupons in raking light, to show differences in surface gloss.

Reflectance and Color

The translucency was examined by Jim Druzik at the Getty Conservation Institute to compare the coupon samples with actual marble. Based on the theory that most light that is not absorbed into a surface is reflected, the % reflectance and L* value for brightness was measured using a spectrophotometer at 550nm. Druzik applied an Ocean Optics spectrophotometer that uses a quartz halogen fiber optic system with a daylight 6500 K illuminant and 10 degree observer. The fillers are ranked from high to low brightness in Table 4. Based on reflectance values, about half

of the putties are brighter than the pure Thassos sample. The fillers giving the most similar value as the pure Thassos includes ground and boiled alabaster. The sulfates are around or brighter than the pure Thassos. The silicates have the greatest range in brightness and the lowest values, Cristobalite and AEROSIL R7200, giving them a more grayish appearance.
The L*a*b* was used to compare the chromaticity between the coupons, whereby a* is the redness-greenness coordinate and b* is the yellowness-blueness coordinate. There is a wide range of a* and b* measurements amongst the coupons which should theoretically enable us to work with a wide palette. The most significant value of chromaticity for the filler coupons for matching actual marble seems to be the yellow-blue coordinate; therefore, the fillers have been ranked by their b* values in Table 4**.**

Some preliminary tests were run on marble to see how the L*a*b* values could be applied in practice. A sample piece of Carrara marble was measured using the same method as the coupons. The L*a*b* values for Cararra did not exactly match the three values for any of the coupons. Focusing first on the L* values, losses were chiseled out of the Carrara, and then filled with the two putty recipes having similar L* values to the stone – cellulose powder and cristobalite. While both had similar values, the cellulose powder made a good match, yet the cristobalite did not. The boiled alabaster putty was chosen independently by the authors from the sample set using an unaided eye, and even though it had a very different L* value as the Carrara, the visual match was very good. This study shows that L* values alone cannot be used to match a marble.

Unlike a spectrophotometer, our eyes are trained to interpret the surface reflectance properties of materials in a psychological way, making the analytical results difficult to correlate with what were are actually seeing. With that challenge in hand, Jim is considering other reflectance techniques using an integrating sphere measurement geometry in order to correlate surface reflectance with total luminous transmittance for visual matching.

Summary of Conclusions

Based on the result of this study, the set of twenty-one different putty recipes have been generally compared for hardness, gloss, color and brightness as shown in Table 4. The preliminary study to find an ideal resin concentration suggests using 60% w/v B-72 in acetone. The maximum amount of filler added to a fixed resin volume has been identified for each filler, which ranged considerably. The hardness values for all of the dried putties were below that of actual pure Thassos marble, however many of them were difficult to carve and may not be appropriate if a lot of finishing needs to be done on the fill. Differences in their working properties have been collected as well as general information about the filler properties (Table 2). The L*a*b* values have allowed the fillers to be ranked by color and brightness, however cannot be directly correlated with the L*a*b* values of actual marble. Half of the putties tested could not obtain a gloss as high as highly polished marble, which may affect the conservator's choice depending on the gloss of a sculpture requiring loss compensation.

This study should facilitate the conservator to fill marble losses that mimic the marble visually, and have appropriate physical properties. without the added need of inpainting. in a way that such knowledge of pigments improves the inpainting process. With the range of results, we should be able to choose an appropriate putty for marble sculptures having varying compositions, condition, or age and without the need for inpainting. For an indoor, white marble in good condition, the fillers that appear to be the most useful in the palette of putties include alabaster powder and boiled alabaster powder due to their reflectance properties, relative softness, high gloss potential, tonality, and working properties. However, this is not to say that mixing fillers or other filler products not included in this study can also produce a good fill for loss compensation. The study is only considered a first phase of what could potentially be an extensive avenue of research.

Further Study

The putties in this study are the beginning of a working palette of fills that would enable the conservator to fill marble losses that mimic the optical properties of marble, and have appropriate physical properties. A knowledge of the filler properties and how they effect B-72 will enable us to pick and choose, much like one would understand a pigment for inpainting. Future work on this phase of the project will include obtaining all the refractive indices of the fillers, and classifying their particle shape and size. Many, but not all of the fillers have been examined using laser granulometry by Assistant Scientist, David Carson, at the Getty Conservation Institute to determine their particle size distribution.

The great complexity involved in a bulked resin system demands a tremendous amount of work yet to be done. It would be beneficial to perform further study on drying rates of these putties. Long-term stability and reversibility of the fills still requires attention. Compressive testing would be useful to study for fills requiring structural strength. With the endless availability of industrial filler products, more filler types could also be compared. Industry has researched surface modifications, such as silanes, coupling agents, anti-skinning agents, as well as additives that improve filler performance. Looking at modified fillers may improve the workability and flexibility of the putty. Furthermore, the fillers could be studied in a different resin system, or even molten B-72 without the use of solvent.

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Instruments

Vickers Hardness Testing Instrument, 40X oculus, 25-500 gram force, Buehler Ltd, 41 Waukegan Rd, Lake Bluff, IL 60044, 847-295-4542

Gloss Meter, Statistical Novo-Gloss, Macbeth Statistical Novogloss

Grinder, MF10 basic, IKA Labortechnik, set at 3000 rpm/min for grinding Thassos marble and alabaster.

Thermolyne Furnace 1400 for baking the Thassos marble.

Paasche Air Eraser Kit, used at 15 psi with medium grit pumice.

Suppliers

Alabaster, Thassos marble, Cararra marble:
Carnivalel and Lohr, Inc., 6251 Clara Street, Bell Gardens, CA 90201, (562) 927-8311

Marblewhite 200, ViCALity Ultra Heavy, Vicron 45-3, ATF 40:
Specialty Minerals, 260 Colombia Street, Adams, MA 01220, (413) 743-0591

Blanc fixe, terra alba, cristobalite, glass flakes, marbledust-M: very fine, calcite, kaolin, alabaster plaster:
Kremer Pigments Inc., 228 Elizabeth Street, New York, NY 10012, (212) 219-2394

Precipitated calcium carbonate, Polywax 2000, Acryloid B-72:
Conservation Support Systems, 924 West Pedregosa Street, Santa Barbara, CA 93101, (805) 682-9843

Pumice (medium):
Conservation Materials (now Conservator's Emporium), 385 Bridgepoint Drive, South St. Paul, Minnesota 55075-2466, (800) 672-1107, fax (651)554-9217

Whatman ashless cellulose powder:
Thomas Scientific, P.O. Box 99, Swedesboro, NJ 08085, (800) 345-2100

Talc: Nicron 400:
TAP Plastics Inc., Dublin, CA 94568, (800) 246-5055, (www.tapplastics.com)

Acematt OK 520, Aerosil COK 84, Aerosil R972, Aerosil R-7200:
Degussa Corporation, 379 Interpace Parkway, Parsippany, NJ 07052, (973) 541-8040

K15 Scotchlite glass bubbles, S22 Scotchlite glass bubbles:
3M, 3M Center, St. Paul, MN 55144-1000, (651) 737-6501

Vaseline petroleum jelly:
Tyco Healthcare/Kendall, 15 Hampshire St., Mansfield, MA 02048

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Recipe #	**Filler**	**(mL)**
	Carbonates	
1	ATF 40	27.5
2	Calcite	35
3	Marbledust-M, very fine	45
4	Marblewhite 200	40
5	Ppt. CaCO3	35
6	Thassos marble - ground (<0.6mm)	40
7	Thassos marble - ground (0.425-0.6mm)	40
8	Thassos marble - ground (0.3-0.425mm)	35
9	Thassos marble - ground (0.15-0.3mm)	35
10	Thassos marble - ground (0.075-0.15mm)	37.5
11	Thassos Marble - baked (<0.6mm)	25
12	ViCALity Ultra Heavy	37.5
13	Vicron 45-3	47.5
	Silicates	
14	Aerosil R-7200	62.5
15	Cristobalite	32.5
16	Glass Flakes	50
17	K15 Scotchlite Glass Bubbles	42.5
18	Talc: Nicron 400	35
	Sulfates	
19	Alabaster plaster	32.5
20	Alabaster ground (<0.6mm)	42.5
21	Alabaster boiled (<0.6mm)	42.5
22	Blanc fixe	32.5
23	Terra Alba	32.5
	Other	
24	Polywax 2000	32.5
25	Whatman Ashless Cellulose Powder	22.5

Table 1. Putty Recipes. The chart shows the amount of filler added to 30mL of 60% w/v Acryloid B-72 in acetone. Each putty recipe is numbered for reference throughout the paper, as all properties and observations are only applicable to this particular ratio of concentrations. If modifications were made to the resin-solvent concentrations, or filler-resin concentrations, the properties would inevitably change.

Table 2. Filler and putty properties.

Filler Composition Supplier	Filler Information health	Putty Observations	Recipe #
ATF 40 96% $CaCO_3$ 1% $MgCO_3$ <0.2% H_2O Specialty Minerals	ATF limestone products are characterized as having high purity, and controlled brightness, particle size and density. This product line is used in tile/sheet flooring, roofing and other building products (Specialty Minerals). Particle size: 0.07 - 0.15 mm (Specialty Minerals) Particle shape: random, crushed (Specialty Minerals) CA Prop 95 carcinogen	-wet putty has a gritty texture -yellowish, mottled surface coloration -has small black inclusions -low polish obtainable (uneven) -hard carvability -high hardness -numerous air bubbles	1
Calcite $CaCO_3$ Kremer (58720)	Calcite can have more than 300 crystal shapes but is generally an irregular, low surface area particle (Katz). It is formed by the crystallization of $CaCO_3$ below 30˚C, and occurs in limestone, marble, and chalk (Solomon). Some manufacturers pretreat the surface with carboxylic acids to make it hydrophobic and neutralize its pH (Solomon). (No surface analysis of the Kremer product has been done at the time of this paper.) Particle size: undetermined as of date	-wet putty has a gummy texture -high polish obtainable -hard carvability -high hardness -numerous air bubbles	2
Marble dust-M, very fine Natural $CaCO_3$ Kremer (59600)	Ground, natural calcium carbonate Particle size: 0-0.6 mm (MSDS)	-wet putty has a gummy texture -high polish obtainable -hard carvability -high hardness -numerous air bubbles	3
MARBLEWHITE 200 96% $CaCO_3$, 1% $MgCO_3$, <0.1% Fe_2O_3, <0.1% H_2O Specialty Minerals	Milled, natural calcite ore that the manufacture processes for greater brightness, and controlled particle size. Particle size: 0.045 - 0.074 mm (Specialty Minerals)	-wet putty has a gummy texture -medium carvability -high polish obtainable -high hardness -numerous air bubbles (hard to fill them)	4

Precipitated Calcium Carbonate $CaCO_3$ Conservation Support Systems	Precipitated calcium carbonates have greater brightness, smaller particles size, greater purity, and higher gloss in resins that natural $CaCO_3$ (Gachter). Particle size: around 0.04 mm	-wet putty has a gummy texture -hard carvability (brittle) -high polish obtainable -low hardness -numerous air bubbles -coupon dried with wrinkled surface	5
Thassos marble $CaCO_3$ $CaMg(CO_3)_2$ Carnivalel & Lohr	Calcium and magnesium carbonate composition was determined at GCI using XRD. Crushed, and sieved. Particle size: <0.6 mm	-wet putty has a gritty texture -hard carvability -low polish (uneven) -high hardness -numerous air bubbles	6
Thassos marble $CaCO_3$ $CaMg(CO_3)_2$ Carnivalel & Lohr	Calcium and magnesium carbonate composition was determined at GCI using XRD. Crushed, and sieved. Particle size: 0.425-0.6 mm	-wet putty has a gritty texture -hard carvability -low polish obtainable (uneven) -high hardness -numerous air bubbles	7
Thassos marble $CaCO_3$ $CaMg(CO_3)_2$ Carnivalel & Lohr	Calcium and magnesium carbonate composition was determined at GCI using XRD. Crushed, and sieved. Particle size: 0.300 - 0.425 micron	-wet putty has a gritty texture -hard carvability -low polish obtainable (uneven) -high hardness -numerous air bubbles	8
Thassos marble $CaCO_3$ $CaMg(CO_3)_2$ Carnivalel & Lohr	Calcium and magnesium carbonate composition was determined at GCI using XRD. Crushed, and sieved. Particle size: 0.150 - 0.300 mm	-wet putty has a gritty texture -hard carvability -low polish obtainable (uneven) -high hardness -numerous air bubbles	9
Thassos marble $CaCO_3$ $CaMg(CO_3)_2$ Carnivalel & Lohr	Calcium and magnesium carbonate composition was determined at GCI using XRD. Crushed, and sieved. Particle size: 0.075 - 0.150 mm	-wet putty has a gritty texture -hard carvability -low polish obtainable -high hardness -numerous air bubbles	10
Thassos marble – baked $CaCO_3$ $CaMg(CO_3)_2$ Carnivalel & Lohr	Calcium and magnesium carbonate composition was determined at GCI using XRD before baking. Chunks of marble were baked for 12 hours at 600˚C. Crushed, and sieved. Particle size: <0.6 mm	-wet putty has a gritty texture -hard carvability -low polish obtainable -high hardness -numerous air bubbles	11

ViCALity Ultra Heavy PCC 60-100% $CaCO_3$ <0.2% H_2O Specialty Minerals	ViCALity Ultra Heavy PCC is a calcitic, precipitated calcium carbonate. Particles have a semi-regular prismatic shape (Specialty Minerals). Particle size: 0.012 mm (Specialty Minerals)	-wet putty has a gummy texture -medium-soft carvability -high polish obtainable -medium hardness -very few air bubbles	12
Vicron 45-3 97% $CaCO_3$ 0.5% $MgCO_3$ <0.1% Fe_2O_3 <0.2% water Specialty Minerals	From natural limestone high in calcium having a controlled particle size and low surface area (Specialty Minerals). Particle size: 0.010 mm average (Specialty Minerals) CA Prop 95 carcinogen	-wet putty has a gummy texture -medium-soft carvability -high polish obtainable -medium hardness -few air bubbles -dry coupon cracked at center	13
Aerosil R-7200 SiO_2 Degussa	Hydrophobic fumed silica coated with methocryloxy functional silane (2-Propenoic acid, 2-methyl-,3-(trimethoxysilyl) propylester). Degussa recommended this product for higher loading levels, and better miscibility in acetone systems. Particle size: 12 nm avg. (Degussa)	-wet putty has a stiff/taffy texture -medium carvability (brittle) -high polish obtainable -soft hardness -numerous air bubbles	14
Cristobalite, very fine SiO_2 Kremer (58689)	Quartz combined with cristobalite and trydimite which are high-temperature polymorphs of quartz commonly found in volcanic rocks. Particle size: 0.008 mm CA Prop 95 carcinogen	-wet putty has a gummy texture -hard carvability -high polish obtainable -soft hardness -numerous air bubbles	15
Glass Flakes SiO_2 Kremer (ZK59852)	Composed of oxides of silicon, aluminum, calcium, boron, and magnesium in an amorphous state. Particle size: unknown as of date	-wet putty has a gummy texture -medium carvability -medium polish obtainable -high hardness -numerous air bubbles	16
K15 Scotchlite Glass Bubbles 97-100% Soda lime borosilicate glass 3% SiO_2, amorphous 3M	3M bubbles are produced by passing glass particles containing a blowing agent, through a flame. Hollow spheres. Particle size: 0.030 – 0.105 mm	-wet putty has a spongy texture -very soft carvability -low polish obtainable -low hardness -numerous air bubbles -hard to sand – too soft, pores trap grit	17

Talc: Nicron 400 Powder MgO-$4SiO_2$-H_20 TAP Plastics	An asbestos-free, hydrated magnesium silicate. Particle size: unknown as of date CA Prop 95 carcinogen	-wet putty has a gummy/stiff texture -soft carvability -low polish obtainable -low hardness -numerous air bubbles (hard to fill them)	18
Alabaster Plaster CaH_4O_6S Kremer (58340)	Calcium sulfate dihydrate, obtained by grinding and separating gypsum that contains about 20% water of crystallization. Particle size: unknown as of date	-wet putty has a gummy texture -soft carvability -high polish obtainable -medium hardness -numerous air bubbles (hard to fill them) -dry coupon had numerous cracks	19
Alabaster, ground $CaSO_4$ Carnivalel and Lohr	Calcium sulfate composition confirmed at GCI using XRD. Crushed and sieved. Particle size: <0.6 mm	-wet putty has a gritty texture -soft carvability -medium polish obtainable -medium hardness -numerous air bubbles	20
Alabaster, boiled $CaSO_4$ Carnivalel and Lohr	Calcium sulfate composition confirmed before boiling using XRD at GCI. Larson recommends heating water-soaked alabaster to increase whiteness before crushing it into powder (1978). Crushed and sieved. Particle size: <0.6 mm	-wet putty has a gritty texture -soft carvability -medium polish obtainable -medium hardness -numerous air bubbles	21
Blanc Fixe $BaSO_4$ Kremer (58700)	Obtained from purified barite having a definite particle size by precipitation (Katz 1978). Particle size: <0.8 mm	-wet putty has a gummy texture -medium carvability -high polish obtainable -low hardness -numerous air bubbles (hard to fill them) -coupon dried with wrinkled surface	22

Terra Alba $CaSO_4 \cdot 2H_2O$ Kremer (58300)	A fully hydrated calcium sulfate or natural gypsum, selenite. Particle size: 0.001–0.07 mm	-wet putty has a gummy texture -medium-soft carvability -medium polish obtainable -high hardness -numerous air bubbles (hard to fill them) -dry coupon had numerous cracks	23
Polywax 2000 $-[CH_2\text{-}CH_2]-_n$ Conservation Support Systems	Polyethlyene (Ethene homopolymer) thoroughly ground in a Krupps coffee grinder. Melting point 126ºC/259ºF (MSDS). Particle size: unknown at this time	-wet putty has a gritty texture -soft carvability (brittle) -medium polish obtainable (uneven) -medium hardness -numerous air bubbles	24
Whatman ashless cellulose powder $C_6H_{10}O_5$ Thomas Scientific	Long chain molecules of cellulose.	-wet putty has a spongy texture -medium-soft carvability -medium polish obtainable -low hardness -numerous air bubbles -hard to sand, too soft, gets dirty	25

Table 3. List of fillers tested and dropped from study.
Note: These fillers were mostly eliminated because of the need to limit the scope of the project, or difficult working properties.

Filler Composition Supplier	Comments
ATF 20 96% $CaCO_3$, 1% $MgCO_3$ Specialty Minerals	ATF 20 has mostly 50 micron particles with less distribution than the ATF 40. Both are a light gray color and have black impurities. Both products appear very similar.
ViCALity Heavy PCC $CaCO_3$ Specialty Minerals	This product was dropped because it was similar to other fillers in the final list, such as precipitated calcium carbonate from Conservation Support Systems.
ViCALity Extra Light PCC $CaCO_3$ Specialty Minerals	The product description says it has a 1.6-1.8 micron scalenohedral particle. It has the lowest density of this product line. It appeared too bright and opaque for this particular study.
Kaolin $H_2Al_2Si_2O_8.H_2O$ Kremer (5925)	Hydrated aluminum-silicate clay. The fill was too highly colored for this study.
Milled Glass Fibers, E-Glass Fibers – Short SiO_2 TAP Plastics	A continuous filament glass having milled fibers. Samples were dark grey, and difficult to mix into the 60% w/v B-72.
Mountain Crystal SiO_2, Kremer (11401)	A quartz powder. Too expensive for wide use. CA Prop 95 carcinogen
S22 Scotchlite Glass Bubbles SiO_2, 3M	The K15 and S22 were very similar in B-72, and since the K15 is used in industry more often, and less expensive, the S22 was eliminated.
Visco-Fill II: Micro Fine Precipitated Silica SiO_2 TAP Plastics	The test putties had numerous bubbles and are very translucent. They were similar to the fumed silica's. Samples tended to crumble.
ACEMATT OK 520	Chemically prepared, precipitated silica manufactured as a matting agent and wax coated. More translucent

SiO_2 Degussa	fills achieved at higher resin concentrations, while opaque at lower resin concentrations. (Perhaps the higher solvent content dissolves the coating?) Coated fillers were avoided in this study.
AEROSIL COK 84 82-86% SiO_2 ,14-18% Al_2O_3 Degussa	A mixture of hydrophilic fumed silica and highly dispersed aluminum oxide in the ratio of 5:1. Samples tended to crumble, and the composition too complicated for this study.
AEROSIL R 972 >99.8% SiO_2 Degussa	A hydrophobic fumed silica coated with dimethyldichlorosilane. Limited concentration of filler could be added to the B-72 without it crumbling, making it too translucent.
CAB-O-SIL 99.8% SiO_2 Degussa	Hydrophilic fumed silica. Tested putties tended to crumble easily.
Fumed Silica SiO_2 Conservation Support Systems	Tested putties tended to crumble easily.
SULFATES	
Calcium sulfate hemihydrate CaSO4.1/2H2O unknown source	Test putties were slow to dry, and highly colored for this particular study
Calcium Sulfate CaO_4S unknown source	Test putties were slow to dry, and highly colored for this particular study.
Marienglas gypseous spar extra fine natural mineral (MSDS) Kremer (11810)	Too expensive for frequent use.

Table 4. Fillers ranked by different properties

Gloss	Hardness	Color b* (Polished)	Brightness L* (Polished)
HIGH GLOSS	SOFT	BLUE	LOW
<u>Blanc Fixe</u>	Aerosil R-7200	Cristobalite	Pure Alabaster
Marbledust-M	K15	Polywax 2000	Aerosil R-7200
Vicron 45-3	Ppt. CaCO3	Pure Thassos	Cristobalite
Calcite	Cristobalite	Cellulose Powder	Pure Carrara
Marblewhite 200	Blanc Fixe	Thassos 0.425-0.6 mm	Terra Alba
Alabaster plaster	Talc	Thassos <0.6 mm	Cellulose Powder
ViCALity Ultra Heavy	Cellulose Powder	Ground Alabaster	Polywax 2000
Ppt. CaCO3	B72	Thassos 0.15-0.3 mm	Talc Nicron 400
Aerosil R-7200	Polywax 2000	Boiled Alabaster	ATF 40
Cellulose Powder	Ground Alabaster	Thassos 0.3-0.425 mm	Thassos <0.6 mm
Ground Alabaster	Boiled Alabaster	Thassos 0.075-0.15 mm	Ground Alabaster
Polywax 2000	Vicron 45-3	Aerosil R-7200	Pure Thassos
Pure Thassos	Glass Flakes	K15	Boiled Alabaster
Boiled Alabaster	Alabaster plaster	Talc Nicron 400	Thassos 0.425-0.6 mm
Terra Alba	ViCALity Ultra Heavy	Glass Flakes	Thassos 0.3-0.425 mm
Thassos 0.075-0.15mm	Marblewhite 200	Vicron 45-3	Thassos 0.15-0.3 mm
Cristobalite	Terra Alba	Calcite	Thassos 0.075-0.15 mm
Baked Thassos	Pure Boiled Alabaster	Baked Thassos	Marbledust-M
ATF 40	Thassos 0.075-0.15 mm	Ppt. CaCO3	Calcite
Talc Nicron 400	Thassos 0.425-0.6 mm	Marbledust-M	Alabaster plaster
Glass Flakes	Thassos 0.15-0.3 mm	Blanc Fixe	Marblewhite 200
Pure Alabaster	Thassos <0.6 mm	Pure Alabaster	Blanc fixe
Thassos <0.6 mm	Marbledust-M	ATF 40	Vicron 45-3
Thassos 0.425-0.6 mm	Calcite	Marblewhite 200	Glass Flakes
Thassos 0.15-0.3 mm	ATF 40	ViCALity Ultra Heavy	Baked Thassos
Thassos 0.3-0.425 mm	Pure Alabaster	Terra Alba	Ppt. CaCO3
K15	Thassos 0.3-0.425 mm	Alabaster Plaster	ViCALity Ultra Heavy
	Baked Thassos		K15
	Pure Baked Thassos		

Pure Thassos

LOW GLOSS	HARD	YELLOW	HIGH