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A NEW CROSS-FLOW MICROFILTRATION MEDIA FOR FINE CLARIFICATION APPLICATIONS

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ABSTRACT

Fine clarification is usually done with either precoated pressure leaf or rotary vacuum filters as well as with disposable cartridge, bag or roll-good filters. All of these require disposal of either precoat or spent cartridge, bags or roll goods, which causes significant costs due to purchase of replacement media, labor as well as disposal costs. As a result, cross-flow microfiltration has made significant inroads into clarification applications, especially with polymeric, ceramic and metal membranes. This paper discusses a new 0.1 μm rated metal cross-flow microfiltration media that is expected to make significant inroads into very fine clarification applications, especially those like titanium oxide particle recovery.

INTRODUCTION

Media for microfiltration, i.e., for filtration of 0.1 to 2 µm size particles in liquids are available commercially in polymers, ceramics and metals. Polymeric membranes can not be used in high chloride environments, extreme pH environments, at temperatures in excess of approximately 200°F and high pressures. Solvents attack polymeric membranes (Cheryan, 1998). The applicability of polymeric membranes is also limited in slurries containing high solids concentration, where the failure may be due to abrasion, or high pressure. The ceramic membranes resolve many of these difficulties. Ceramic membranes are strong but brittle, and must be sealed using polymeric seals. The temperatures and corrosive environments that the seals can withstand limit the use of ceramic membranes. Ceramic membranes have low fracture toughness; therefore, back-pulsing or thermal cycling may introduce cracks, and the cracks may propagate rapidly leading to final brittle failure. Sintered metal media address the concerns described above with ceramic and polymeric membranes. Metal media have higher fracture toughness, high thermal shock resistance and are weldable. The sintered metal media are available in different alloys to handle wide-ranging corrosion environments.

Disposal of polymeric membranes, bags, roll goods and ceramic media often poses an environmental problem, and disposal of contaminated media is difficult and expensive. The sintered metal filters are cleanable, either in-place or by external chemical cleaning. Depending on the nature of the contaminant, the sintered metal filters are completely recyclable.

This paper describes the physical and mechanical properties of 0.1 µm grade sintered metal media in Hiflow™ Nickel, 316L SS (Stainless Steel) and Hastelloy® C-22. New manufacturing technology developments have enabled the manufacture of highly permeable sintered metal media, with fine porosity and high pore volume fraction. While Hiflow™ Nickel media will provide higher flow during filtration, Stainless Steel and Hastelloy media have been developed for corrosive liquids.

SINTERED METAL MICROFILTRATION MEDIA PROPERTIES

Sintered metal filtration media are prepared by selecting specific particle size distribution of metal or alloy particles, molding or pressing into specific shape and sintering them at high temperature and controlled environment. For most iron and nickel base alloys, (i.e. stainless steels and nickel based superalloys and Hastelloy), the sintering is performed either in vacuum or hydrogen or other reducing environment to develop high sintered strength and ductility. For consistent manufacturing of the sintered metal media, the bubble point pressure and air permeabilities of the media are controlled within specified ranges.

Table 1: Physical Properties of Sintered Metal Microfiltration Media

ott rade	aterial	ube Inner iameter nches)	/all hickness nches)	orosit	ensile trength si)
1 µm	iflow™ Ni	35	090	[illegible]	000

Strength and Microstructure

A novel manufacturing process, proprietary to Mott Corporation, is applied to fabricate Hiflow™ Nickel media that has high pore volume fraction and fine porosity for 0.1 µm particle filtration (Jha and Rubow, 1999). The pore volume fraction in Hiflow Nickel media is approximately 40%. This high level has not been obtained previously in sintered porous metal media for industrial liquid filtration. Figure 1 shows a scanning electron micrograph of the Hiflow Nickel media. The flow

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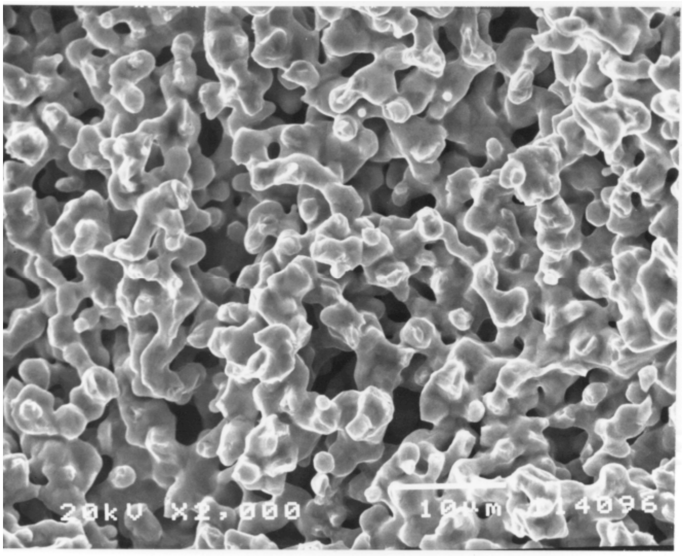
pores are tortuous in nature and flow path lengths are long. Therefore, even though the pore dimensions on the porous surface appear to be micrometer size due to high surface roughness, the finer subsurface pores, high tortuosity and long flow paths provide effective obstacle to the passage of sub-micron particles through the media. The micrograph in Figure 1 shows that the metal powder particles used to fabricate the media are well sintered providing intrinsically high mechanical strength.

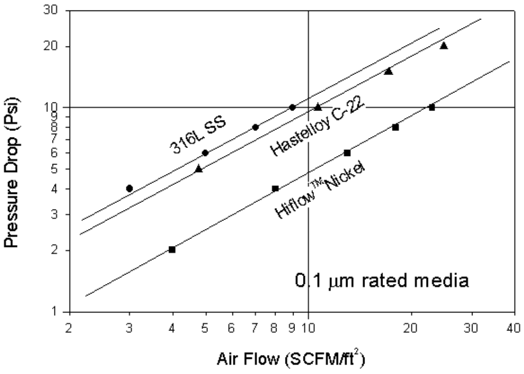
Table 1 shows the tensile strength of the media, typical dimensions and porosity fraction. The strong media can be back-pulsed to dislodge the particle cake formed during fluid filtration and increase the permeate flow. The high media strength provides a high collapse strength (> 1000 psi for 0.5” outer diameter, 24” long tube) and burst pressure. The high strength aids in the construction of robust filter modules, which can be operated at high pressures and temperatures approaching 300°C, depending on the application.

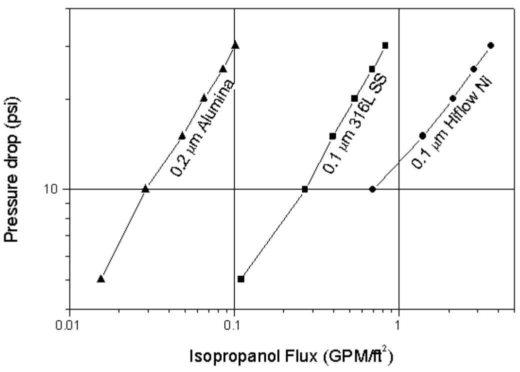
Clean Flow Permeability

Figures 2 and 3 show the gas and liquid permeabilities of 0.1 µm grade sintered metal media. The clean liquid permeabilities of Hiflow Nickel and 316L SS media are considerably higher than that of the 0.2 µm grade alumina membrane. The permeability of 0.1 µm grade Hiflow Nickel is considerably higher than that of similarly graded 316L SS or Hastelloy C-22 due to the higher porosity in the Hiflow Nickel media.



igure 1: Scanning Electron Micrograph of



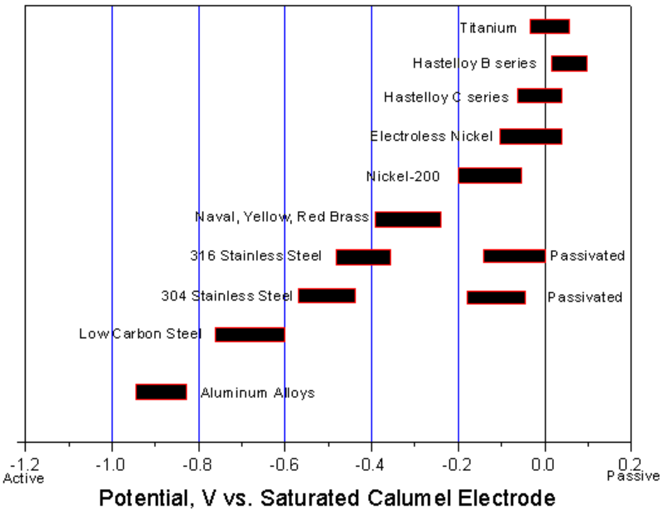


igure 2: Nitrogen Ga ermeability of Sintered Meta

igure 3: Isopropanol ermeability of Sintered Metal

Corrosion Resistance

Figure 4 shows the galvanic series of various common metals and alloys depicting their relative corrosion resistance. The corrosion guidelines for Hiflow Nickel media are based upon the exposure of wrought Nickel 200 metal (UNS N02200). Figure 4 shows that the corrosion potential of Nickel in 5% NaCl solution is comparable to that of passivated stainless steels (Fontana, M.G., 1986). A porous material will have a higher corrosion rate than a corresponding solid material of the same chemistry due to its high exposed surface area. In the case of Nickel, in general, reducing conditions retard corrosion attack, whereas oxidizing conditions promote corrosion. Nickel porous materials can be used in handling bromine, halogen gases, and chlorinated solvents. Nickel is used widely in the food processing industry. Nickel is resistant to neutral and mild acidic solutions, but is readily attacked by oxidizing acids, such as nitric acid. Alkaline solutions and mild atmospheric conditions do not affect Nickel. Nickel has limited corrosion resistance in seawater and brackish water.



gure 4: Galvanic Series of Metals and Alloys in 5% NaCl Solution

FILTRATION OF TITANIUM DIOXIDE SLURRY

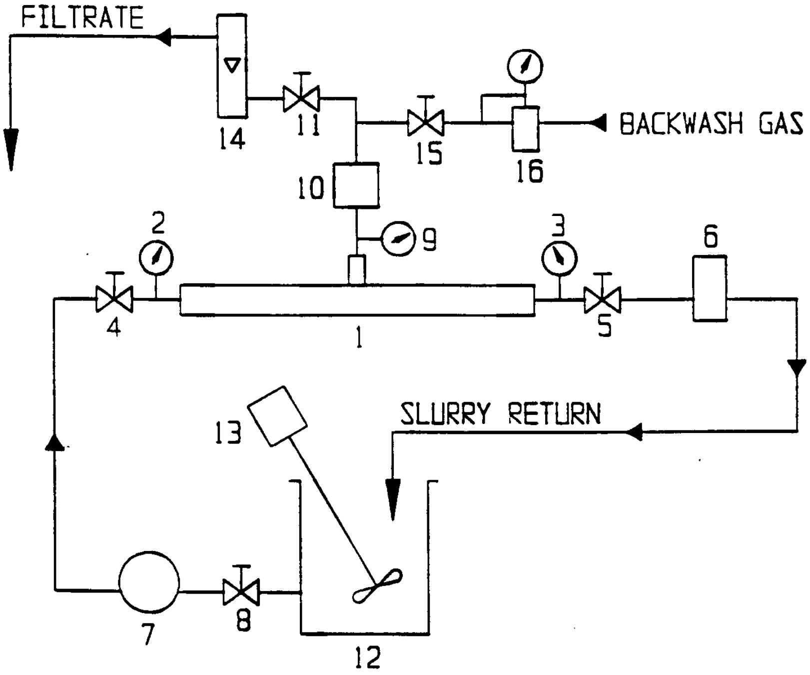
Titanium dioxide particles are produced in very high volumes, and have a myriad of applications in industrial and consumer products. They are widely used in paints, and often sold as concentrated slurry. Cross-flow filtration of titanium dioxide slurry has been used to concentrate up to 50 to 80% (Trendell et. al., 1997). Wastewater recovery of titanium dioxide particle containing waste is also of potential interest. Previous attempts for barrier filtration of TiO_2 particles at Mott's R&D laboratory were unsuccessful and the particles were found to readily coat and plug the filter media. Successful cross-flow filtration of TiO_2 slurry has now been demonstrated with 0.1 µm Hiflow Nickel and 316L SS media and the results are discussed below.

Experimental Details

Figure 5 is a schematic diagram of the cross-flow test stand used for filtering TiO_2 slurry. 0.1 µm grade Hiflow Nickel and 316L SS media were used to perform the filtration tests. The pore volume fraction of the two media is considerably different, as listed in Table 1. The purpose of the test was to evaluate filtration characteristics, backwash efficiency and the steady state flow characteristics of the media.

Actual plant wastewater slurries of titanium dioxide particles were received from DuPont. Horiba Laser Scattering Particle Size Analyzer was used to determine the particle size distribution in the slurry. The filtrate quality was determined by measuring filtrate turbidity, as well as by measuring weight gain on a membrane filter, (i.e., Total Suspended Solids, TSS). Scanning electron microscopy coupled with energy dispersive X-ray analysis was used to determine nature of the particles loaded on the filtration media.

A concentrated slurry of 1 wt.% titanium dioxide was made by suspending reagent grade titanium dioxide particles in tap water. A surfactant was used to keep the slurry de-flocculated. The pH of the slurry was 6.8, and at this pH, the particles have been found to remain well-dispersed (Marchant and Wakeman, 1997). The cross-flow velocity in all tests was maintained at 10 ft./sec. Table 2 shows the particle size distribution in various titanium dioxide slurries tested.



1. MOTT CAT No. 7000 LSX
2. INLET PRESSURE GAUGE
3. OUTLET PRESSURE GAUGE
4. INLET CONTROL VALVE
5. OUTLET CONTROL VALVE
6. FLOWMETER
7. PUMP
8. PUMP SHUT-OFF VALVE
9. FILTER PRESSURE GAUGE
10. FILTRATE RESERVOIR
11. FILTRATE CONTROL VALVE
12. FEED TANK
13. AGITATOR
14. FILTRATE FLOWMETER
15. BACKWASH VALVE
16. BACKWASH REGULATOR

gure 5: Schematic Diagram of Cross-Flow Filter

RESULTS

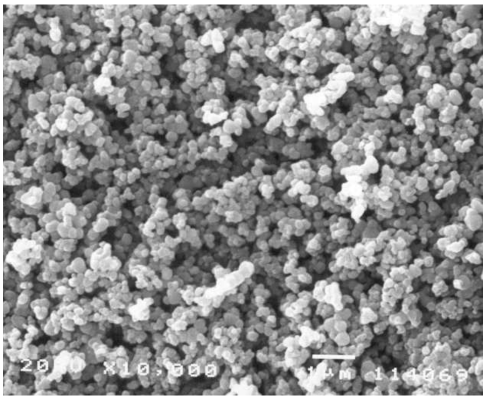
Figure 6 shows a scanning electron micrograph of the titanium dioxide particles collected on a membrane filter. The particles are spherical in shape and the particle sizes are quite uniform. The concentration of DuPont wastewater sample was 30 ppm by weight and a 1wt. % slurry was made in the lab using tap water to simulate a concentrated slurry. The pH of both wastewater as well as the 1wt.% slurry ranged from 6 to 7. Adding 5 ml of surfactant to ten liters of wastewater sample did not change the pH. The slurry temperature during testing ranged from 70 to 90°F.

The slurry turbidity changed as the cross-flow filtration test progressed. Initially, the turbidity of well-mixed slurry was 617 NTU. As the tests progressed, titanium dioxide particles settled on the solid surfaces, as well as cake on the filter surface, and slurry turbidity would drop to 47 NTU in about 18 hours. Upon back washing, the slurry turbidity would increase to 250 to 350 NTU. The filtrate quality was determined by measuring turbidity and total suspended solids (TSS). The results are as follows:

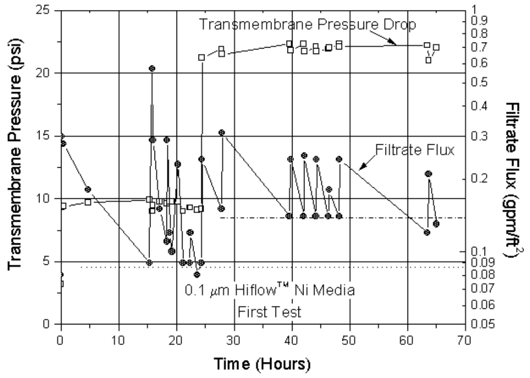
TSS in Filtrate immediately after backwash:	0.103 ppmw
Turbidity of filtrate:	0.15 to 0.2 NTU

TSS in Filtrate over one backwash cycle: 0.0134 ppmw

Table 2: Particle size distribution in titanium dioxide slurries					
mple		mber Based Distribution			
sizes in μm	.% solids	edian	an	Dvn	nimum
Slurry in Tap Water	vt.%	48	34	21	39
astewater Sample 1	ppmw	85	11	38	50
astewater Sample 1 with surfactant	ppmw	82	05	29	5
astewater Sample 2	ppmw	7	36	37	97



igure 6: SEM Micrograph of



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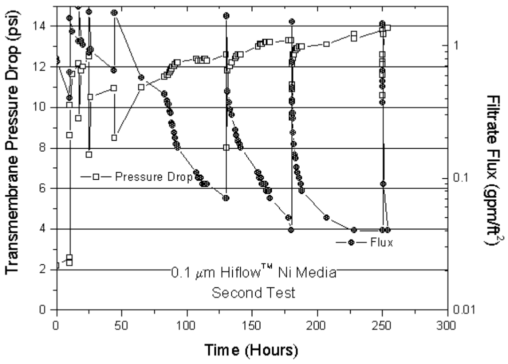
ure 7: Cross-Flow test data



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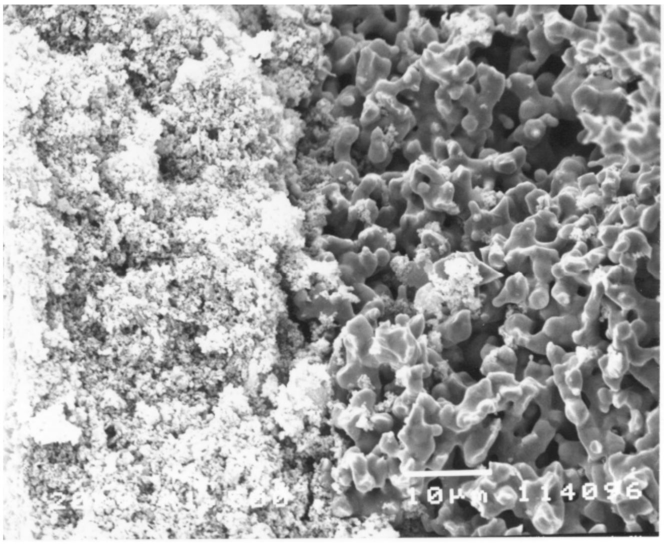
ure 8: Cross-Flow Test data

Figure 7 shows the applied trans-membrane pressure (TMP) and filtrate flux as a function of time with the first wastewater sample. Initially the filtrate flux was high at 0.3 gpm/ft^2 at 10 psi TMP. Over a fifteen hour run, the flux declined to 0.09 gpm/ft^2. A 50-psi back pulse restored the flux, but flux attenuated to 0.1 gpm/ft^2 within 3 hours. This prompted application of more frequent back pulse (at two-hour intervals). After the media was conditioned, the flux attenuated to less than 0.1 gpm/ft^2 within two hours at 10 psi TMP. Increasing the TMP to 25 psi increased the average flux to 0.15 gpm/ft^2.

A second longer-term test was performed with a new sample of titanium dioxide wastewater stream. Figure 8 shows the trans-membrane pressure and filtrate flux as a function of test time. The trans-membrane pressure was held between 10 to 15 psi, and the system was back washed after every 48 hours. The data show that while the initial flux is high, after the media conditions, the flux may drop to as low as 0.04 gpm/ft^2 in 48 hours. It was possible to recover the flux by back

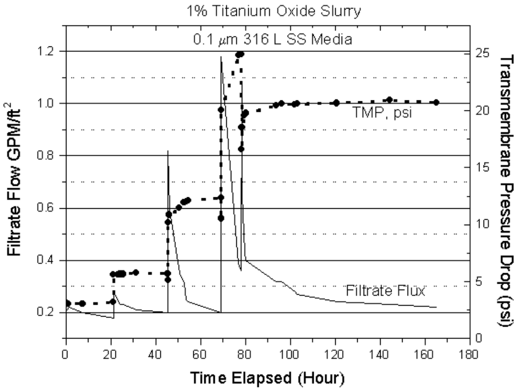


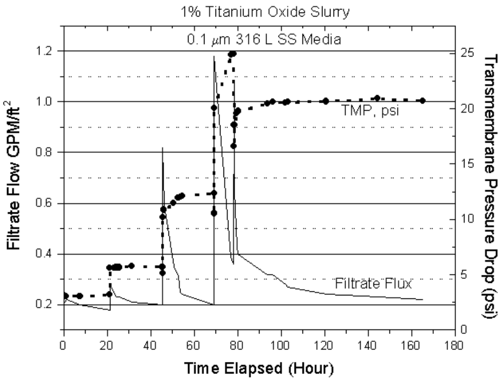
gure 9: TiO$_2$ cake on Hiflow Nickel Media

pulsing, but the flux attenuated to low values within 5 to 10 hours. The back pulse pressure was 50 psi.

After completing the cross-flow filtration trials, the filter media was sectioned to determine the mechanism for flow deterioration. The cut section showed that a thin and rigid titanium dioxide cake had formed on the media surface. Figure 9 shows a SEM photomicrograph of the cake structured supported on the porous media. The cake is approximately 50 µm thick, and a few titanium dioxide particles have penetrated approximately 20 µm deep into the media. Most of the filtration was actually occurring at the cake surface. The cake surface is rather dense and therefore reduces permeability. If the media is not back-pulsed frequently, a rigid cake structure forms, which is not readily broken at 50-psi back-pulse pressure. Therefore, to maintain high flux, the media should be back pulsed as frequently as possible.

To further explore the filtration behavior of sintered metal microfiltration media, a 1wt.% titanium dioxide slurry in tap water was tested in re-circulation mode. Both Hiflow™ Nickel and 316L Stainless Steel media, rated for 0.1 µm filtration, were tested. Figures 10 and 11 show permeate flux and associated trans-membrane pressure drop observed during the cross-flow filtration tests with Hiflow™ Nickel and 316L SS media, respectively. The cross-flow filtration was started at low TMP, and then TMP was increased to 20 – 25 psi. E
blowback. The data shows that permeate flow recov





gure 11: Cross-flow Filtration data on
% TiO$_2$ Slurry

gure 10: Cross-flow Filtration data on
% TiO$_2$ Slurry

turbidity with both media was less than 1 NTU. The results on Hiflow Nickel media show that there is a slight dependence of the steady state permeate flux on the TMP. The steady state permeate flux through 316L SS media was somewhat independent of the TMP. At a TMP of 22 psi, the steady state permeate flux through the 0.1 μm Hiflow Nickel media was twice that through the 0.1 μm 316L SS media. This is primarily due to the difference in the porosity of the two media. A more porous media in general is expected to show higher flux and better response to blowback.

SUMMARY

Tests were conducted to determine the applicability of sintered metal microfiltration media in clarifying slurries with small amounts of sub-micrometer size particulate matter. The results show that the sintered metal microfiltration media can perform the clarification efficiently at acceptable throughput levels. The use of sintered metal media will provide permanent filtration systems, which will need to be maintained in-frequently. Using coagulants and flocculents would further improve the throughput and filtration efficiency.

Sintered metal microfiltration media have been used for wastewater recovery and other industrial liquid/solid separation processes for a long time. The benefits of using sintered metal media are their long life, low maintenance, and predictable behavior. Advances in manufacturing processes have enabled the development of 0.1 μm grade media with high porosity fraction, enabling high throughput and reduced media fouling. Sintered metal microfiltration media have been developed in various alloys, namely Nickel, Stainless Steel and Hastelloy C-22 for application in increasingly corrosive environments. The sintered metal media are completely weldable; therefore, the temperature and corrosion resistance of the seals does not limit the applications.

Sintered metal microfiltration media would be an excellent material for pre-filtering the wastewater streams, before the water is purified using ultra and nanofiltration grade polymeric membranes. The sintered metal media can remove the hard particles that would damage the membranes. Membrane modules located downstream of the sintered metal cross-flow filters would remove solutes or higher molecular weight materials.

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