MÁRCIA MARIA SALGADO LOPES BASSO

EVALUATION OF THE PERFORMANCE AND DURABILITY OF BUILDING PAINTS PRODUCED WITH WASTE FROM GRANITE AND MARBLE PROCESSING

Thesis submitted to the Civil Engineering Graduate Program of the Universidade Federal de Viçosa in partial fulfillment of the requirements for the degree of *Doctor Scientiae.*

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Leonardo Gonçalves Pedroti
Adviser

To my parents,
Márcio and Maria José,
to my sister Mírian, and
to my husband Alan.

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ABSTRACT

BASSO, Márcia Maria Salgado Lopes, D.Sc., Universidade Federal de Viçosa, June, 2024. **Evaluation of the performance and durability of building paints produced with waste from granite and marble processing**. Adviser: Leonardo Gonçalves Pedroti. Co-advisers: José Carlos Lopes Ribeiro and José Maria Franco de Carvalho.

The production of paints using waste from the granite and marble processing is a new alternative to promote sustainable development in civil construction. However, challenges such as the lack of an effective process for dispersing and stabilizing pigments, along with the low resistance of mixtures to attack by biological agents, can compromise the performance or even make the use of these paints unfeasible. Therefore, this study aimed to evaluate the performance and durability properties of latex paints produced from the combination of polyvinyl acetate (PVA) resin and granite (GW) and marble (MW) waste, with a focus on proposing improvements in the formulation. To achieve this purpose, the most appropriate proportions of GW and MW (pigments), water (solvent), and PVA resin (binder) were initially determined to meet the minimum requirements for hiding power and abrasion resistance established for economic category paints. Next, the influence of biocidal and dispersant additives on paint performance was investigated, analyzing hiding power, abrasion resistance, dispersion, and resistance to bacterial growth. Finally, the durability of paints produced with GW and MW was evaluated, comparing them with economic category latex paints available on the market through exposure tests to natural and accelerated weathering. The results obtained indicated that paints with the best performance are composed of 41-47% GW, 35% water, and 18-24% resin. Furthermore, the inclusion of a biocidal additive maintained the optical and mechanical properties of the paints, while substantially reducing the bacteria growth. However, the addition of a dispersant additive improved the dispersion of the components, but compromised the abrasion resistance and durability of the paint. The weathering results demonstrated that the paints only underwent color alteration after one year of exposure. Comparisons of the effects of natural and accelerated weathering indicated that paint deterioration observed after one year of natural weathering can be reproduced in just two cycles (16.6 days) of accelerated weathering. It is concluded that paints produced with granite waste exhibit great potential for use due to their performance and durability compared to other economical paints.

Keywords: Durability. Granite. Marble. Paints. Performance. Waste.

RESUMO

BASSO, Márcia Maria Salgado Lopes, D.Sc., Universidade Federal de Viçosa, junho de 2024. **Avaliação do desempenho e da durabilidade de tintas para construção produzidas com resíduos provenientes do beneficiamento do granito e do mármore.** Orientador: Leonardo Gonçalves Pedroti. Coorientadores: José Carlos Lopes Ribeiro e José Maria Franco de Carvalho.

A produção de tintas a partir de resíduos do beneficiamento de granito e mármore é uma nova alternativa para promover o desenvolvimento sustentável na construção civil. Contudo, desafios como a falta de um processo eficaz para dispersão e estabilização de pigmentos, aliado à baixa resistência das misturas ao ataque de agentes biológicos, podem comprometer o desempenho ou até mesmo inviabilizar o uso dessas tintas. Portanto, este estudo objetivou avaliar as propriedades de desempenho e durabilidade de tintas látex produzidas a partir de resina de poliacetato de vinila (PVA) e resíduos de granito (GW) e mármore (MW), com foco em propor melhorias na formulação. Para atingir esse objetivo, inicialmente foram determinadas as proporções mais adequadas de GW e MW (pigmentos), água (solvente) e resina PVA (ligante) para atender aos requisitos mínimos de poder de cobertura e resistência à abrasão estabelecidos para tintas de categoria econômica. Em seguida, foi investigada a influência dos aditivos biocidas e dispersantes no desempenho da tinta, analisando o poder de cobertura, a resistência à abrasão, a dispersão e a resistência ao crescimento bacteriano. Por fim, avaliou-se a durabilidade das tintas produzidas com GW e MW, comparando-as com tintas látex de categoria econômica disponíveis no mercado através de testes de exposição ao intemperismo natural e acelerado. Os resultados obtidos indicaram que as tintas com melhor desempenho são compostas por 41-47% GW, 35% água e 18-24% resina. Além disso, observou-se que a inclusão do aditivo biocida mantém as propriedades ópticas e mecânicas das tintas, reduzindo substancialmente o crescimento de bactérias. Contudo, a adição do aditivo dispersante, apesar de promover a dispersão dos componentes, compromete a resistência à abrasão e a durabilidade da tinta. Os resultados de intemperismo demonstram que as tintas só sofreram alteração de cor em um ano de exposição. Comparando o intemperismo natural e o acelerado, fica evidente que foi possível reproduzir a deterioração da pintura de um ano de intemperismo natural em apenas dois ciclos (16,6 dias) de intemperismo acelerado. Conclui-se que as tintas produzidas com resíduo de granito, apresentam grande potencial de utilização, devido ao seu desempenho e durabilidade em comparação com outras tintas econômicas.

Palavras-chave: Durabilidade. Granito. Mármore. Tintas. Desempenho. Resíduo.

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SUMMARY

GENERAL INTRODUCTION

1. INITIAL CONSIDERATIONS

The construction sector is one of the major contributors to job creation and economic growth in a country. However, its production processes consume a significant amount of natural resources and generate substantial volumes of solid waste, resulting in a series of environmental impacts (ALALOUL *et al.*, 2022; BOHNENBERGER *et al.*, 2018; NOROUZI *et al.*, 2021). According to Benachio, Freitas and Tavares (2020), the construction industry is responsible for over 30% of the extraction of natural resources, as well as 25% of solid waste generated in the world.

Therefore, recent studies have been conducted to evaluate new alternatives that promote sustainable development in construction. These alternatives primarily focus on reducing the use of natural resources, minimizing waste on construction sites, and utilizing various types of industrial waste in the manufacture of new construction materials (LIMA *et al.*, 2021).

Among the industrial sectors that generate large amounts of solid waste, the ornamental stone processing industry stands out, generating millions of tons of waste annually worldwide (CORCIONE *et al.*, 2018; GADIOLI *et al.*, 2022; REBELLO *et al.*, 2019). According to the Brazilian Association of the Ornamental Stone Industry (ABIROCHAS, 2023), Brazil belongs to the group of large producers and exporters of ornamental rocks, focusing primarily on marble and granite. Thus, many studies on the use of this waste in the manufacture of new construction materials have already been developed, including the production of concrete (ABOUELNOUR *et al.*, 2024; GENCEL *et al.*, 2022; GHORBANI *et al.*, 2018; JAIN; GUPTA; CHAUDHARY, 2019, 2020; KORE; VYAS; KABEER, 2020; LI *et al.*, 2022; OSTROWSKI *et al.*, 2020; PEREIRA; CAPUZZO; LAMEIRAS, 2022; TUNC, 2019), mortars (ALMADA; SANTOS; SOUZA, 2022; AMARAL *et al.*, 2020; AMIN *et al.*, 2020; AZEVEDO *et al.*, 2019; GEHLOT; SHRIVASTAVA, 2023; LOZANO-LUNAR *et al.*, 2020; NASCIMENTO *et al.*, 2020; CHOUHAN *et al.*, 2019); cements (LI *et al.*, 2013; MEDINA *et al.*, 2017), and ceramics (COELHO *et al.*, 2022; AZEVEDO *et al.*, 2021; GADIOLI *et al.*, 2022; XAVIER *et al.*, 2019). However, the amount of waste used in these projects is still insignificant compared to the amount generated, highlighting the necessity for its application in other studies (VIJAYALAKSHMI; SEKAR; GANESH PRABHU, 2013).

In recent years, studies have suggested the use of granite and marble waste in building paints as a new alternative capable of reducing the amount of waste deposited in the environment, in addition to contributing to the development of a more economical and sustainable product. Lopes *et al*., (2019) studied the application of granite waste, acting as a pigment, in low-cost latex paints, while Tressmann *et al*., (2020) conducted a similar study, using marble waste instead of granite waste. Promising results were obtained in these studies regarding the performance of paints produced with these types of wastes.

Waste generated from the processing of ornamental rocks consists of fine-grained rock fragments obtained during the cutting and polishing of slabs. Granite waste is composed of a high percentage of silica, which contributes to improving the mechanical properties of paints, such as resistance to abrasion and scratching, as observed by Lopes *et al.* (2019), in addition to providing superhydrophobic properties and chemical durability to coatings (AHMED *et al.*, 2015; BOZORG; RAMEZANI, 2017). On the other hand, marble waste presents calcium carbonate ($CaCO_3$) in its composition, which improves the covering power of the coatings, as verified by Tressmann *et al.* (2020). All these characteristics enhance the use of these residues in the production of paints.

Despite this, this sustainable approach remains relatively unexplored. Future studies still need to be developed to improve the composition of these paints and their manufacturing process to obtain paints with properties similar to those of commercial paints. Lopes *et al.* (2019) highlighted the need to improve the preparation of pigments and the use of additives that give the paints certain performance and durability properties. Tressmann *et al.* (2020) observed the presence of fungi and bacteria in paints produced with marble waste, indicating a significant amount of organic matter within the paint components or contamination during the manufacturing process.

In light of this context, this work aimed to propose new improvements in the composition of latex paints produced with polyvinyl acetate (PVA) resin alongside pigments derived from granite and marble waste, in addition to evaluating their performance and durability, aiming to develop a product that is technically proficient and economically feasible for application in civil construction.

2. OBJECTIVES

The general objective of this work is to evaluate the performance and durability properties of PVA latex paints produced with waste generated from the processing of granite and marble, considering proposals for improvements in the paint formulation.

Specific objectives include:

- Define the most appropriate proportions of granite and marble waste (pigments), water (solvent), and PVA (resin) capable of meeting the minimum hiding power and abrasion resistance requirements defined for PVA latex paint belonging to the economic category.
- Evaluate the influence of biocidal and dispersant additives on the performance of paints produced with granite and marble waste, assessing their hiding power, abrasion resistance, dispersion, and resistance to the growth of fungi and bacteria.
- Evaluate the durability of granite and marble waste paints and compare them with commercially available paints of the economic category, based on tests of paints exposed to accelerated weathering and natural weathering.

3. JUSTIFICATION

According to Yurdakul (2020), the industrial production of ornamental stones has experienced significant global growth in recent years. Brazil generates around 2.5 million tons of fine waste per year, the majority of which comes from the granite and marble industries (ABIROCHAS, 2023; ALMEIDA *et al.*, 2023).

Vijayalakshmi, Sekar, and Ganesh Prabhu (2013) reported that during different stages of processing granite rocks, the amount of waste generated reaches around 20 to 25% of global production. In the case of marble, Rana *et al.* (2016) state that the waste content represents around 30 to 50% of the total volume of blocks processed. Consequently, thousands of tons of waste are generated per year in Brazil.

Improper disposal of this waste harms the environment and human health. Depositing it in landfills involves high transportation costs and requires large areas and environmental control (ALVES; ESPINOSA; TENÓRIO, 2015). The proposal to incorporate these wastes in the manufacture of new products aims, among other factors, to reduce the cost of manufactured products and contribute to the preservation of the environment.

Granite and marble wastes consist largely of rock fragments, with chemical, physical, mechanical, and mineralogical characteristics suggesting that these materials can be used as pigments in paint production (LOPES *et al*., 2019).

Lopes *et al*. (2019) and Tressmann *et al*. (2020) have already studied the production and performance of paints based on granite waste and marble waste, respectively. These authors observed that granite waste has a great influence on the mechanical properties of paints, while marble waste interferes, especially, with the optical properties of the products. Furthermore, Lopes *et al*. (2019) and Tressmann *et al*. (2020) highlighted factors that could harm the performance or even make the use of paints unfeasible, such as the lack of an efficient process for dispersing and stabilizing pigments, and the low resistance of the mixtures to attack by fungi and bacteria, resulting in a short shelf life of the bottled paint. Therefore, new studies are needed to address the composition, production, performance, and durability of paints based on granite and marble waste, both separately and in combination.

Checking the performance and durability of paint films containing granite and marble waste, as well as comparing them with paints available on the market, are necessary procedures to attest to the quality and technical viability of the product. Only this investigation can encourage ornamental stone processing and civil construction companies to use granite and marble waste as a viable alternative.

It is also important to highlight that Brazil is among the five largest paint markets in the world, with building paints responsible for 82% of total production (ABRAFATI, 2022). Despite being an essential construction material for the durability and aesthetics of buildings, it remains largely inaccessible to the poor. Therefore, this research is also justified by the proposal to develop an economical paint, aimed mainly at low-income populations, especially those living near sources of granite and marble waste.

4. NOVELTY

In recent decades, sustainable development has been considered one of the main challenges in the construction industry. As a result, professionals from various fields seek solutions to reduce the environmental impacts generated by constructions, and numerous studies have already been published on this subject.

Regarding construction materials, studies on the incorporation of waste into concretes, mortars, and ceramic materials already have consolidated conclusions and diversified applications. However, polymeric materials, such as sustainable paints, still lack attention.

According to Schieweck and Bock (2015) and Xiong *et al*., (2013), commonly available paints generate various environmental impacts, as many contain organic solvents that release volatile organic compounds (VOCs). Additionally, pigments may contain toxic substances that can harm living organisms when present in high concentrations (MOREIRA; MOREIRA, 2004). For these reasons, paints are considered potential pollutants of the environment and indoor air quality of buildings, affecting human health, especially during the construction phase of a building.

Previous works that have developed paints with lower environmental, social, and economic impact (AZEVEDO, 2018; GALVÃO *et al.,* 2018; LOPES *et al.,* 2019; TRESSMANN *et al*., 2020) respectively used waste from the kaolin processing industry, iron ore tailings, waste from granite processing, and waste from marble processing.

In line with this research, the present work aims to develop a sustainable paint based on waste generated from granite and marble processing. It also seeks to propose improvements in the composition of the paints to achieve satisfactory performance and durability. The novelty of this work lies in the absence of studies in the literature that simultaneously evaluate the application of waste from granite and marble in paint production. Additionally, durability tests need to be explored to study the feasibility of using these paints as substitutes for those commonly found on the market.

5. WORK STRUCTURE

This work is divided into five sections, as follows:

• *General introduction:* this section comprises initial considerations necessary to contextualize this work; general and specific objectives; justification for carrying out this study; novelty of this research and structuring of this work.

• *Article 1:* use of statistical design of quaternary mixtures to optimize the performance of building paints based on waste from granite and marble processing. In this chapter, viscosity, hiding power of dry paint, and resistance to wet abrasion without abrasive paste were evaluated through experimental design of mixtures to define the ideal range of variation for each component, depending on the performance results.

• *Article 2:* influence of biocidal and dispersant additives on the performance of paints containing waste from granite and marble processing. In this chapter, paints were evaluated in terms of viscosity, hiding power of dry paint, resistance to wet abrasion without abrasive paste, dispersion, and resistance to the growth of fungi and bacteria through an experimental design of quaternary mixtures, in order to define the ideal variation range of additives, depending on the performance results.

• *Article 3:* evaluation of the durability of paints containing waste from granite and marble processing. In this chapter, formulations obtained in the previous studies were subjected to natural and accelerated weathering tests to simulate the behavior of these paints in real-world conditions. Furthermore, a comparison was made between the durability of these paints and economic category paints available on the market.

• *General conclusions:* presents the final considerations and recommendations for future works.

REFERENCES

ABIROCHAS. **Balance of rock exports and imports in the 1st quarter of 2023**. 2023. https://abirochas.com.br/wp-content/uploads/2023/06/Informe-01_2023-Balanc%CC%A7o-1o-trimestre-2023.pdf. .

ABOUELNOUR, M. A.; EL-AZIZ, M. A. A.; OSMAN, K. M.; FATHY, I. N.; TAYEH, B. A.; ELFAKHARANY, M. E. Recycling of marble and granite waste in concrete by incorporating nano alumina. **Construction and Building Materials**, vol. 411, p. 134456, jan. 2024. https://doi.org/10.1016/j.conbuildmat.2023.134456.

ABRAFATI. **O Setor de Tintas no Brasil**. 2022. Available in: https://abrafati.com.br/setor-de-tintas/dados-do-setor/.

AHMED, N.M.; MOHAMED, M.G.; MABROUK, M.R.; ELSHAMI, A.A. Novel anticorrosive pigments based on waste material for corrosion protection of reinforced concrete steel. **Construction and Building Materials**, vol. 98, p. 388–396, nov. 2015. DOI 10.1016/j.conbuildmat.2015.08.111.

ALALOUL, W. S.; MUSARAT, M. A.; RABBANI, M. B. A.; ALTAF, M.; ALZUBI, K. M.; AL SALAHEEN, M. Assessment of Economic Sustainability in the Construction Sector: Evidence from Three Developed Countries (the USA, China, and the UK). **Sustainability**, vol. 14, nº 10, p. 6326, 22 maio 2022. https://doi.org/10.3390/su14106326.

ALMADA, B. S.; SANTOS, W. J. dos; SOUZA, S. R.. Marble and granite waste as mineral addition in mortars with different water-cement ratios. **Ambiente Construído**, vol. 22, nº 4, p. 7–22, dez. 2022. https://doi.org/10.1590/s1678-86212022000400624.

ALVES, J. O.; ESPINOSA, D. C. R.; TENÓRIO, J. A. S. Recovery of steelmaking slag and granite waste in the production of rock wool. **Materials Research**, vol. 18, nº 1, p. 204–211, 2015. https://doi.org/10.1590/1516-1439.324414.

AMARAL, L. F.; DELAQUA, G. C. G.; NICOLITE, M.; MARVILA, M. T.; DE AZEVEDO, A. R. G.; ALEXANDRE, J.; VIEIRA, C. M. F.; MONTEIRO, S. N. Eco-friendly mortars with addition of ornamental stone waste - A mathematical model approach for granulometric optimization. **Journal of Cleaner Production**, vol. 248, p. 119283, mar. 2020. DOI 10.1016/j.jclepro.2019.119283.

AMIN, S. K.; ALLAM, M. E.; GARAS, G. L.; EZZ, H. A study of the chemical effect of marble and granite slurry on green mortar compressive strength. **Bulletin of the National Research Centre**, vol. 44, nº 1, 2020. https://doi.org/10.1186/s42269-020-0274-8.

AZEVEDO, G. Use of the Reply of Caulim'S Benefiting Industries for the Production of Earth-Based Ecological Ink. **Tecnologia em Metalurgia, Materiais e Mineração**, vol. 15, nº 3, p. 242–247, 2018.

BENACHIO, G. L. F.; FREITAS, M. do C. D.; TAVARES, S. F. Circular economy in the construction industry: A systematic literature review. **Journal of Cleaner Production**, vol. 260, p. 121046, Jul. 2020. https://doi.org/10.1016/j.jclepro.2020.121046.

BOHNENBERGER, J. C.; PIMENTA, J. F. de P.; ABREU, M. V. S.; COMINI, U. B.; CALIJURI, M. L.; MORAES, A. P. de; PEREIRA, I. da S. Identificação de áreas para implantação de usina de reciclagem de resíduos da construção e demolição com uso de análise multicritério. **Ambiente Construído**, vol. 18, nº 1, p. 299–311, 2018. https://doi.org/10.1590/s1678-86212018000100222.

BOZORG, M.; RAMEZANI, A. Characterization and protective performance of acrylic-based nanocomposite coating reinforced with silica nanoparticles. **Materials and Corrosion**, vol. 68, nº 7, p. 725–730, 2017. https://doi.org/10.1002/maco.201609347.

COELHO, A. M. R.; SAGGIORO, F. G.; SALES JUNIOR, J. C. C.; ANDRADE, J. C. S.; CAVALCANTE, R. H. Evaluation of the potential use of granite waste in products of the red ceramic industry in the state of Amazonas. **Matéria (Rio de Janeiro)**, vol. 27, nº 2, 2022. https://doi.org/10.1590/s1517-707620220002.1309.

CORCIONE, C. E.; PALUMBO, E.; MASCIULLO, A.; MONTAGNA, F.; TORRICELLI, M. C. Fused Deposition Modeling (FDM): An innovative technique aimed at reusing Lecce stone waste for industrial design and building applications. **Construction and Building Materials**, vol. 158, p. 276–284, 2018. DOI 10.1016/j.conbuildmat.2017.10.011.

ALMEIDA, K. M. de; GADIOLI, M. C. B.; SAGRILLO, V. P. D.; DE AGUIAR, M. C. Industrial Scale Manufacturing of Red Ceramic Sealing Blocks with Ornamental Stone Wastes. **Revista de Gestão Social e Ambiental**, vol. 17, nº 10, p. e04141, 11 out. 2023. https://doi.org/10.24857/rgsa.v17n10-015.

AZEVEDO, A. R. G. de; MARVILA, M. T.; BARROSO, L. da S.; ZANELATO, E. B.; ALEXANDRE, J.; XAVIER, G. de C.; MONTEIRO, S. N. Effect of Granite Residue Incorporation on the Behavior of Mortars. **Materials**, vol. 12, nº 9, p. 1449, 5 maio 2019. DOI 10.3390/ma12091449.

AZEVEDO, M. C. de; MARVILA, M. T.; DELAQUA, G. C. G.; AMARAL, L. F.; COLORADO, H.; VIEIRA, C. M. F. Economy analysis of the implementation of extruded tiles fabrication in a ceramic industry containing ornamental rock waste. **International Journal of Applied Ceramic Technology**, , p. ijac.13728, 11 mar. 2021. DOI 10.1111/ijac.13728.

GADIOLI, M. C. B.; DE AGUIAR, M. C.; VIDAL, F. W. H.; SANT'ANA, M. A. K.; ALMEIDA, K. M. de; GIORI, A. J. N. Incorporation of Ornamental Stone Waste in the Manufacturing of Red Ceramics. **Materials**, vol. 15, nº 16, p. 5635, 16 ago. 2022. https://doi.org/10.3390/ma15165635.

GALVÃO, J. L. B.; ANDRADE, H. D.; BRIGOLINI, G. J.; PEIXOTO, R. A. F.; MENDES, J. C. Reuse of iron ore tailings from tailings dams as pigment for sustainable paints. **Journal of Cleaner Production**, vol. 200, p. 412–422, 2018. https://doi.org/10.1016/j.jclepro.2018.07.313.

GEHLOT, M. R.; SHRIVASTAVA, S.. Utilization of stone waste in the development of sustainable mortar: A state of the art review. **Materials Today: Proceedings**, mar. 2023. https://doi.org/10.1016/j.matpr.2023.03.149.

GENCEL, O.; NODEHI, M.; YAVUZ BAYRAKTAR, O.; KAPLAN, G.; BENLI, A.; KOKSAL, F.; BILIR, T.; SIDDIQUE, R.; OZBAKKALOGLU, T. The use of waste marble for cleaner production of structural concrete: A comprehensive experimental study. **Construction**

and Building Materials, vol. 361, p. 129612, dez. 2022. https://doi.org/10.1016/j.conbuildmat.2022.129612.

GHORBANI, S.; TAJI, I.; TAVAKKOLIZADEH, M.; DAVODI, A.; DE BRITO, J. Improving corrosion resistance of steel rebars in concrete with marble and granite waste dust as partial cement replacement. **Construction and Building Materials**, vol. 185, p. 110–119, 2018. DOI 10.1016/j.conbuildmat.2018.07.066.

JAIN, A.; GUPTA, R.; CHAUDHARY, S. Performance of self-compacting concrete comprising granite cutting waste as fine aggregate. **Construction and Building Materials**, vol. 221, p. 539–552, 2019. DOI 10.1016/j.conbuildmat.2019.06.104.

JAIN, A; GUPTA, R; CHAUDHARY, S. Sustainable development of self-compacting concrete by using granite waste and fly ash. **Construction and Building Materials**, vol. 262, p. 120516, 2020. DOI 10.1016/j.conbuildmat.2020.120516.

KORE, S. D.; VYAS, A. K.; KABEER, S. A. A brief review on sustainable utilisation of marble waste in concrete. **International Journal of Sustainable Engineering**, vol. 13, nº 4, p. 264–279, 3 jul. 2020. DOI 10.1080/19397038.2019.1703151.

LI, Y.; YU, H.; ZHENG, L.; WEN, J.; WU, C.; TAN, Y. Compressive strength of fly ash magnesium oxychloride cement containing granite wastes. **Construction and Building Materials**, vol. 38, p. 1–7, 2013. DOI 10.1016/j.conbuildmat.2012.06.016.

LI, Z.; LAO, J.; WANG, L.; LIM, N. S.; TAN, K. H.; QIAN, S. A review on substitution of natural sand with granite fines in sustainable concrete. **Construction and Building Materials**, vol. 346, p. 128417, set. 2022. DOI 10.1016/j.conbuildmat.2022.128417.

LIMA, L.; TRINDADE, E.; ALENCAR, L.; ALENCAR, M.; SILVA, L. Sustainability in the construction industry: A systematic review of the literature. **Journal of Cleaner Production**, vol. 289, p. 125730, mar. 2021. https://doi.org/10.1016/j.jclepro.2020.125730.

LOPES, M. M. S.; ALVARENGA, R. C. S. S.; PEDROTI, L. G.; RIBEIRO, J. C.; CARVALHO, A. F.; CARDOSO, F. de P.; MENDES, B. C. Influence of the incorporation of granite waste on the hiding power and abrasion resistance of soil pigment-based paints. **Construction and Building Materials**, vol. 205, p. 463–474, 2019. https://doi.org/10.1016/j.conbuildmat.2019.02.046.

LOZANO-LUNAR, A.; DUBCHENKO, I.; BASHYNSKYI, S.; RODERO, A.; FERNÁNDEZ, J. M.; JIMÉNEZ, J. R. Performance of self-compacting mortars with granite sludge as aggregate. **Construction and Building Materials**, vol. 251, p. 118998, 2020. DOI 10.1016/j.conbuildmat.2020.118998.

MEDINA, G.; SÁEZ DEL BOSQUE, I. F.; FRÍAS, M.; SÁNCHEZ DE ROJAS, M. I.; MEDINA, C. Granite quarry waste as a future eco-efficient supplementary cementitious material (SCM): Scientific and technical considerations. **Journal of Cleaner Production**, vol. 148, p. 467–476, 2017. https://doi.org/10.1016/j.jclepro.2017.02.048.

MOREIRA, F. R.; MOREIRA, J. C. Lead kinetics in human body and its significance to health. **Ciência & Saúde Coletiva**, vol. 9, nº 1, p. 167–181, 2004. .

NASCIMENTO, A. S.; DOS SANTOS, C. P.; DE MELO, F. M. C.; OLIVEIRA, V. G. A.; BETÂNIO OLIVEIRA, R. M. P.; MACEDO, Z. S.; DE OLIVEIRA, H. A. Production of plaster mortar with incorporation of granite cutting wastes. **Journal of Cleaner Production**, vol. 265, p. 121808, ago. 2020. DOI 10.1016/j.jclepro.2020.121808.

NOROUZI, M.; CHÀFER, M.; CABEZA, L. F.; JIMÉNEZ, L.; BOER, D. Circular economy in the building and construction sector: A scientific evolution analysis. **Journal of Building Engineering**, vol. 44, p. 102704, dez. 2021. https://doi.org/10.1016/j.jobe.2021.102704.

OSTROWSKI, K.; STEFANIUK, D.; SADOWSKI, Ł.; KRZYWIŃSKI, K.; GICALA, M.; RÓŻAŃSKA, M. Potential use of granite waste sourced from rock processing for the application as coarse aggregate in high-performance self-compacting concrete. **Construction and Building Materials**, vol. 238, p. 1–14, 2020. https://doi.org/10.1016/j.conbuildmat.2019.117794.

PEREIRA, M. M. L.; CAPUZZO, V. M. S.; LAMEIRAS, R. de M. Evaluation of use of marble and granite cutting waste to the production of self-compacting concrete. **Construction and Building Materials**, vol. 345, p. 128261, ago. 2022. https://doi.org/10.1016/j.conbuildmat.2022.128261.

RANA, A.; KALLA, P.; VERMA, H. K.; MOHNOT, J. K. Recycling of dimensional stone waste in concrete: A review. **Journal of Cleaner Production**, vol. 135, p. 312–331, 2016. DOI 10.1016/j.jclepro.2016.06.126.

REBELLO, T. A.; ZULCÃO, R.; CALMON, J. L.; GONÇALVES, R. F. Comparative life cycle assessment of ornamental stone processing waste recycling, sand, clay and limestone filler. **Waste Management and Research**, vol. 37, nº 2, p. 186–195, 2019. https://doi.org/10.1177/0734242X18819976.

SCHIEWECK, A.; BOCK, M. C. Emissions from low-VOC and zero-VOC paints - Valuable alternatives to conventional formulations also for use in sensitive environments? **Building and Environment**, vol. 85, p. 243–252, 2015. DOI 10.1016/j.buildenv.2014.12.001.

CHOUHAN, H. S.; KALLA, P.; NAGAR, R.; GAUTAM, P. K. Influence of dimensional stone waste on mechanical and durability properties of mortar: A review. **Construction and Building Materials**, vol. 227, p. 116662, dez. 2019. DOI 10.1016/j.conbuildmat.2019.08.043.

TRESSMANN, D. M. G. A.; PEDROTI, L. G.; DE CARVALHO, A. F.; RIBEIRO, J. C. L.; CARDOSO, F. P.; LOPES, M. M. S.; DE OLIVEIRA, A. F.; FERREIRA, S. O. Research into the use of marble waste as mineral filler in soil pigment-based paints and as an active pigment in waterborne paints. **Construction and Building Materials**, vol. 241, p. 117976, 2020. DOI 10.1016/j.conbuildmat.2019.117976.

TUNC, E T. Recycling of marble waste: A review based on strength of concrete containing marble waste. **Journal of Environmental Management**, vol. 231, p. 86–97, fev. 2019. DOI 10.1016/j.jenvman.2018.10.034.

VIJAYALAKSHMI, M.; SEKAR, A. S.S.; GANESH PRABHU, G. Strength and durability properties of concrete made with granite industry waste. **Construction and Building Materials**, vol. 46, p. 1–7, 2013. DOI 10.1016/j.conbuildmat.2013.04.018.

XAVIER, G. de C.; AZEVEDO, A. R. G. de; ALEXANDRE, J.; MONTEIRO, S. N.; PEDROTI, L. G. Determination of Useful Life of Red Ceramic Parts Incorporated with Ornamental Stone Waste. **Journal of Materials in Civil Engineering**, vol. 31, nº 2, p. 04018381, 2019. https://doi.org/10.1061/(asce)mt.1943-5533.0002590.

XIONG, J.; WANG, L.; BAI, Y.; ZHANG, Y. Measuring the characteristic parameters of VOC emission from paints. **Building and Environment**, vol. 66, p. 65–71, 2013. DOI 10.1016/j.buildenv.2013.04.025.

YURDAKUL, M. Natural stone waste generation from the perspective of natural stone processing plants: An industrial-scale case study in the province of Bilecik, Turkey. **Journal of Cleaner Production**, vol. 276, p. 123339, dez. 2020. https://doi.org/10.1016/j.jclepro.2020.123339.

ARTICLE 1.

OPTIMIZATION OF PERFORMANCE OF BUILDING PAINTS USING GRANITE AND MARBLE WASTE[1]

ABSTRACT

The production of paints using waste from granite and marble processing is a new alternative to contribute to sustainable development in civil construction. However, the lack of studies on the composition and performance of these paints makes the dissemination of this new construction material unfeasible. Therefore, this study aims to investigate the composition of these paints using statistical tools to obtain products with performance compatible with technical regulations and commercial paints. The paint formulations were defined through a quaternary mixture planning. The solids content, pH, viscosity, hiding power, and abrasion resistance were determined for all samples. The paints produced with granite waste showed better hiding power and abrasion resistance, as granite waste has a finer granulometry, in addition to being predominantly composed of silica. Finally, the paints produced in this study and the commercial paints showed similar behavior, which supports the use of waste from the processing of ornamental rocks in paint production.

Keywords: Building paint. Granite waste. Industrial residue. Marble waste. Quaternary mixture design. Recycling.

1. INTRODUCTION

Due to the accelerated growth of the civil construction sector, the global market for paints and coatings was valued at around 137,100 million dollars in 2021, with an annual growth rate of more than 4% expected for the coming years (MORDOR INTELLIGENCE, 2022). According to the Brazilian Association of Paint Manufacturers (ABRAFATI, 2022),

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Brazil ranks among the world's top five largest paint markets, along with China, the United States, India, and Japan. In 2021, Brazil's paint production exceeded 1.7 billion liters, with architectural paints constituting over 80% of the total volume. These countries collectively represent major players in the global paint industry, showcasing substantial production and consumption levels.

Paints are complex mixtures comprising organic and inorganic pigments, binding vehicles, thinner vehicles and additives. The production of paints involves the use of various chemicals, resulting in high concentrations of organic compounds, suspended solids, colored materials, and hazardous pollutants such as heavy metals (ANIYIKAIYE *et al.*, 2019; MANDAL *et al.*, 2020). The environmental impacts associated with the production, use, and disposal of paints necessitate the exploration of more sustainable alternatives to improve their technical performance and develop coatings that are environmentally acceptable.

Previous experimental studies by Myint, Zakaria and Ahmed (2010), Alam and Alandis (2011), Moreno *et al.* (2014) and Bal *et al.* (2017) reported some examples of experimental studies that sought to use more sustainable resins for the production of paints. Saxena and Dhimole (2006), Legodi and de Waal (2007), Ahmed *et al.* (2015), Cardoso *et al.* (2016), Galvão *et al.* (2018), Lopes *et al.* (2019), Tressmann *et al.* (2020) and Silva *et al.* (2017) studied more sustainable alternatives for replacing active and inert pigments conventionally used in paint production. In most of these studies, the solvent of the paints was water rather than organic solvents to reduce the emission of volatile organic compounds (VOCs) (OU *et al.*, 2022).

Lopes *et al.* (2021a), Lopes *et al.* (2021b), Lopes *et al.* (2019) used granite waste as pigments for low-cost latex paints, and Tressmann *et al.* (2020) developed similar research using marble processing waste instead of granite waste. Promising results were obtained in these studies regarding the technical performance of the paints produced with these types of wastes.

Waste generated during ornamental stone processing consists of fine particles obtained from cutting and polishing rock blocks (ALMADA *et al.*, 2020; GHANNAM; NAJM; VASCONEZ, 2016; NASCIMENTO *et al.*, 2021). China, India and Brazil are major generators of granite and marble waste. Annually, Brazil produces millions of tons of ornamental stones, including significant amounts of granite and marble (ABIROCHAS, 2021; SINGH; NAGAR; AGRAWAL, 2016a). Similarly, China and India have thriving industries in the extraction and processing of these stones, leading to substantial waste generation. However, when not disposed of correctly, granite and marble waste can cause significant environmental impacts such as soil and water contamination. It is crucial to prioritize proper waste management practices, including recycling, reuse, and responsible disposal, to mitigate these environmental effects. By implementing sustainable approaches, these countries can minimize the adverse impacts associated with granite and marble waste and promote a more environmentally friendly stone processing industry (BACARJI *et al.*, 2013; SOUZA *et al.*, 2017).

Granite waste, in particular, contains a high percentage of silica (SiO_2), which enhances the mechanical properties of paints, such as abrasion and scratch resistance (LOPES *et al.*, 2019), while also imparting superhydrophobic properties and chemical durability to coatings (AHMED *et al.*, 2015; BOZORG; RAMEZANI, 2017). Marble waste, on the other hand, contains calcium carbonate ($CaCO_3$), contributing to the hiding power of coatings (TRESSMANN *et al.*, 2020). These characteristics make these waste materials attractive for use in paint production.

However, the combined effects of granite and marble waste on the technical performance of sustainable paints have not been investigated in previous literature. Consequently, the potential synergistic effects between these waste types on the optical and mechanical properties of paints remain unknown. Furthermore, there is a need to optimize the composition of these sustainable paints to ensure they meet technical regulations.

In this context, optimization techniques play a crucial role in enhancing the characteristics and efficiency of products, processes, or methods to make them more sustainable. Variables influencing experimental performance can be categorized as process variables or mixture variables (ONG *et al.*, 2019). Mixture design methods enable comprehensive and systematic studies of how different mixture components' proportions affect performance, offering significant potential for optimization (NOVAES et al., 2018; LI et al., 2021). Despite this potential, mixture design methods are infrequently employed in optimization applications due to their complexity in visualizing and interpreting high-dimensional systems (FALLEH *et al.*, 2019; SYAFITRI; SARTONO; GOOS, 2015).

Therefore, the main objective of this research is to use a quaternary mixture design to optimize the composition of paints produced with distinct types of wastes from ornamental stone processing to obtain a performance compatible with technical regulations and with commercial paints. The following original contributions were provided by this work to the state-of-the-art: (a) The study proposes the use of accessible and cost-effective materials for paint production. These materials encompass water as a solvent, polyvinyl acetate resin as a binder, in addition to granite and marble waste as pigments/mineral fillers. (b) It offers new insights into the combined use of granite and marble waste in paint production, an area that was not previously explored in sustainable construction. (c) For the first time, systematic comparisons between paints made of granite waste and marble waste were provided. (d) It presents a practical application of the quaternary mixture design approach, an underutilized tool, to determine the optimal proportions of the fundamental components of the developed construction material. (e) The study includes equations that model the performance of the proposed paints based on their basic components, predicting the behavior of the sustainable material in terms of viscosity, hiding power, and abrasion resistance. These equations also enable an optimization of these properties and the refinement of the paint formulation.

2. MATERIAL AND METHODS

2.1. Materials

The pigments consisted of waste generated from granite and marble processing, obtained through the diamond wire cutting process and subjected to a pre-treatment. In line with the aim of sustainability, water was chosen as the solvent due to its abundance and environmentally friendly nature compared to conventional organic solvents. As for the binder, polyvinyl acetate resin (PVA) was selected for its low cost, water solubility, and easy availability in the market. Notably, the inclusion of additives commonly used in the paint industry was intentionally omitted due to their challenging procurement and high cost.

2.2. Methodology

2.2.1. Pre-treatment of granite and marble wastes

After being collected, the granite and marble wastes were separately submitted to a pre-treatment. These wastes were dried outdoors, crushed and sieved through an 8-mesh sieve (2.38 mm opening) to remove larger particles and homogenize the material. The pigments were prepared sequentially, based on the method developed by (CARDOSO *et al.*, 2016), which consists of the disaggregation and dispersion of the particles in an aqueous medium using a Cowles disk coupled to a mechanical stirrer at 1500 rpm. Subsequently, the wastes in an aqueous medium were passed through an 400- mesh sieve (0.038 mm opening).

2.2.2. Characterization of granite and marble wastes

The wastes were characterized after being submitted to the pre-treatment. The following parameters were evaluated for physical characterization of the wastes: granulometric distribution curve, using a Bettersize 2000 laser particle size analyzer in the range of 0.02 μm to 2000 μm; specific gravity, using a Le Chatelier's volumetric flask, according to NBR16605 (ABNT, 2017); specific surface area by the BET method; and organic matter content by burning at 440 ºC, based on NBR13600 (ABNT, 2022). Scanning electron microscope (SEM) images were obtained with a Leo 1430VP equipment for morphological characterization.

For chemical characterization, the materials were subjected to pH measurements according to the EMBRAPA (2017) and X-ray Fluorescence (XRF) using the Shimadzu Micro-EDX-1300 spectrometer, applying a high voltage (50 keV and 50 μA) and mapping 1200 points. For mineralogical characterization and identification of crystalline structures, X-ray Diffraction (XRD) was performed in a D8 Discover diffractometer (Bruker), using CuKα radiation (1.5418 Å) and 2θ ranging from 3° to 70°.

2.2.3. Experimental program

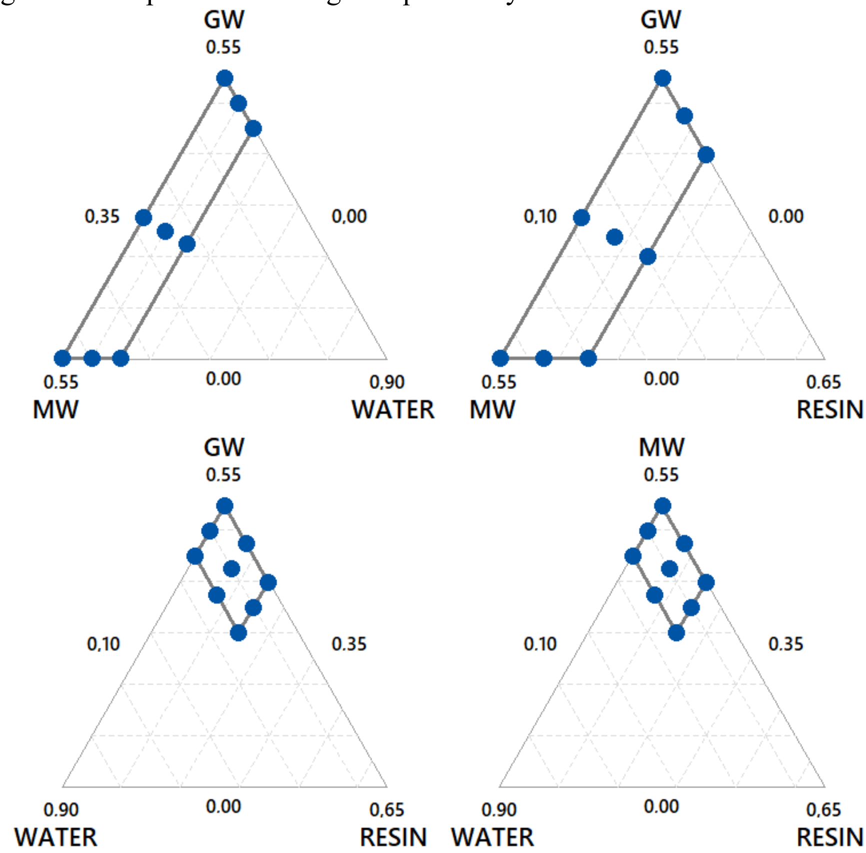
This research was based on an experimental design of mixtures with four components (quaternary), which allows for studying and optimizing the response variables as a function of four independent variables. The independent variables of the mixture design were the granite waste (GW) and marble waste (MW) pigments, ranging from 0 to 55% by mass; resin, ranging from 10 to 25% by mass, considering the volatile and non-volatile parts; and water, ranging from 35 to 45% by mass. These variation ranges were defined based on the studies developed by Lopes et al. (2019) and Tressmann et al. (2020). It should be noted that the variation range of water content was defined to ensure that the paint maintains adequate viscosity for proper application. This is aimed at preventing issues such as paint running (resulting from low viscosity) and the formation of an excessively thick paint film (caused by high viscosity) (LOPES et al., 2019). In addition, the relationship between the mass of resin and pigment is compatible with the values adopted in PVA latex paints found on the market, which can vary between 10 and 43% (SILVA; UEMOTO, 2005). Table 1.1 and Figure 1.1 show the 35 formulations defined in the present experimental program, using the Minitab® 17 statistical analysis software, after selecting a design in extreme vertices of degree three, augmented by axial and central points.

Table 1.1- Proportions of paints designed in the Minitab® 17 statistical analysis software.

Id.	GW	MW	Water	Resin	Id.	GW	MW	Water	Resin
GW55.0%	0.55	0	0.35	0.1	GW10.6%+MW38.1%	0.106	0.381	0.375	0.138
GW50.0%	0.5	0	0.4	0.1	GW10.6%+MW33.1%	0.106	0.331	0.425	0.138
GW47.5%	0.475	0	0.35	0.175	GW10.6%+MW30.6%	0.106	0.306	0.375	0.213
GW45.0%	0.45	0	0.45	0.1	GW10.6%+MW25.6%	0.106	0.256	0.425	0.213
GW42.5%	0.425	0	0.4	0.175	GW15.0%+MW15.0%	0.15	0.15	0.45	0.25
GW40.0%	0.4	0	0.35	0.25	GW17.5%+MW17.5%	0.175	0.175	0.4	0.25
GW37.5%	0.375	0	0.45	0.175	GW18.8%+MW18.8%	0.188	0.188	0.45	0.175
GW35.0%	0.35	0	0.4	0.25	GW20.0%+MW20.0%	0.2	0.2	0.35	0.25
GW30.0%	0.3	0	0.45	0.25	GW21.3%+MW21.3%	0.213	0.213	0.4	0.175
MW55.0%	0	0.55	0.35	0.1	GW22.5%+MW22.5%	0.225	0.225	0.45	0.1
MW50.0%	0	0.5	0.4	0.1	GW23.8%+MW23.8%	0.238	0.238	0.35	0.175
MW47.5%	0	0.475	0.35	0.175	GW25.0%+MW25.0%	0.25	0.25	0.4	0.1
MW45.0%	0	0.45	0.45	0.1	GW25.6%+MW10.6%	0.256	0.106	0.425	0.213
MW42.5%	0	0.425	0.4	0.175	GW27.5%+MW27.5%	0.275	0.275	0.35	0.1
MW40.0%	0	0.4	0.35	0.25	GW30.6%+MW10.6%	0.306	0.106	0.375	0.213
MW37.5%	0	0.375	0.45	0.175	GW33.1%+MW10.6%	0.331	0.106	0.425	0.138
MW35.0%	0	0.35	0.4	0.25	GW38.1%+MW10.6%	0.381	0.106	0.375	0.138
MW30.0%	0	0.3	0.45	0.25	-	-	-	-	-

Note - Id.: sample identification; GW: granite waste; MW: marble waste.

Figure 1.1- Experimental design of quaternary mixture defined in Minitab® 17.



2.2.4. Production and determination of paint performance characteristics and properties

To produce the paints, appropriate contents of granite and/or marble waste pigments were mixed with water and PVA resin according to the components' mass proportions defined in the statistical design. The mixing process was carried out with a Cowles disc coupled to a mechanical stirrer at a speed of 400 rpm.

The paint samples were tested for viscosity, solids content, hiding power of the dry paint, and resistance to wet abrasion without abrasive paste. The kinematic viscosity was measured from the flow time of the fluid, in seconds, using a Ford cup viscometer with orifice No. 4, according to NBR5849 (ABNT, 2015). The apparent and plastic viscosities were determined using a Couette rotational viscometers (Fann Model 35 viscometers), based on ISO10414-1 (ISO, 2008). The solids content was calculated as the ratio of the oven-dried paint mass and the initial paint mass, according to D 3723-05 (ASTM, 2017). The hiding power of the dry paint was calculated as the maximum applied area (m^2) per unit volume of paint (L), so that the coverage has a contrast ratio of 98.5%, based on D 2805-11 (ASTM, 2018) and NBR14942 (ABNT, 2019a). The resistance to wet abrasion without abrasive paste was given by the number of cycles a paint film can resist until wear at least 80% of the area traversed by the brush, as recommended by D 4060-19 (ASTM, 2019) and NBR15078 (ABNT, 2006).

All these characterization and performance tests were also carried out on eight economic category latex paints available on the Brazilian market. Thus, additional comparisons were made between the properties of paints based on granite and marble waste and commercial paints.

2.2.5. Statistical analysis

Based on the paint characterization and performance results, polynomial models (regression equations) were generated, considering the significance level of the terms (p-value < 0.05). The parameters used to optimize the performance of the paints were hiding power (target value of 4 m^2/l) and abrasion resistance (target value of 100 cycles) for the economic latex paint category, according to NBR 15079-1 (ABNT, 2019b).

The mixture proportions associated with the best performance were determined using the statistical desirability function and the modeling of response surfaces. The individual desirability function (*di*), which varies from 0 to 1, was calculated according to Equation 1, when the goal was to maximize the results. In this equation, y is the response, L is the minimum value (considered as zero), *T* is the target value (assumed 4 m²/L for hiding power and 100 cycles for abrasion resistance), and *s* is the weight (assuming 1, either for hiding power and abrasion resistance).

$$d_i = \begin{cases} 0 \; se \; y < L \\ \left(\frac{y-L}{T-L}\right)^s \; se \; L \leq y \leq T \\ 1 \; se \; y > T \end{cases} \qquad \text{(Equation 1)}$$

In addition, the global desirability (*D*), which also varies from 0 to 1, was calculated as the geometric mean of individual desirabilities (*di*), according to Equation 2, in which *m* is the number of responses studied in the optimization process. Zero means an unacceptable value, and 1 (one) is related to the most desirable value. All of these statistical analyzes were performed using the Minitab® 17 software.

$$D = \sqrt[m]{d_1 . d_2 \dots d_m} \qquad \text{(Equation 2)}$$

2.2.6. Microscopic analyzes

Some granite and marble waste paints and commercial paints were selected for microscopic analysis of paint films. Microscopic images of the paints were taken using the Leo 1430VP scanning electron microscope. In this situation, SEM stubs were painted with three coats of paint.

In addition, the roughness of the paint films was determined using a 3D optical profilometer, model Contour GTK, adopting the *"Ra"* parameter. In this case, the substrates were glass slides painted with three coats of paint. The roughness was determined in the central part of the film. These measurements were performed in three different regions of the sample, and the average value was then calculated.

3. RESULTS AND DISCUSSION

3.1. Characterization of pigments

Figure 1.2 shows the particle size distribution curves of the pigments, and Table 1.2 shows the results of the physical characterization, organic matter content and pH of these materials.

Figure 1.2– Particle size distribution curves of granite waste and marble waste pigments.

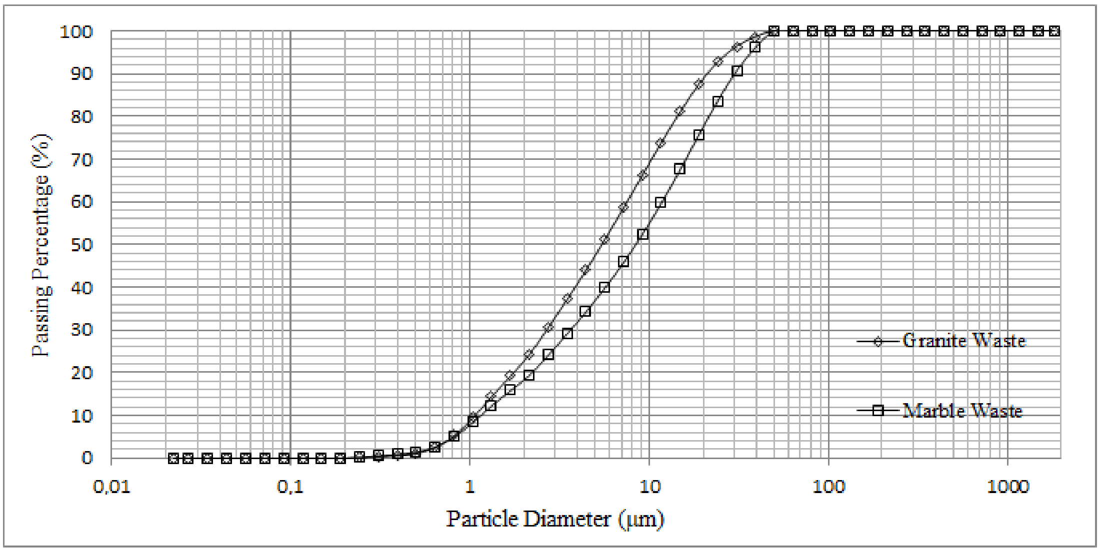


Table 1.2- Physical and chemical characterization of the pigments.

Pigment	Specific gravity (g/cm³)	Specific surface area (m²/g)	Diameter (µm)			Organic matter content (%)	pH
			D10	D50	D90		
Granite waste	2.60	6.11	1.20	6.31	26.09	0.55	8.89
Marble waste	2.82	4.42	1.30	9.99	37.85	0.20	9.52

Note: D10: indicates the maximum diameter exhibited by 10% of the particles; D50: corresponds to the maximum diameter exhibited by 50% of the particles; D90: corresponds to the maximum diameter exhibited by 90% of the particles.

The wastes had an average diameter lower than 10 µm. As per the values of D10 and D90, the range of variation in the size of particles from granite and marble waste is between 1µm and 40 µm. According to Diebold et al. (2022), the particle sizes of mineral fillers used in paint formulations generally cover the range of 0.01 to 45 µm, although most are between 0.5

and 10 μm. In paint formulation, particle size influences coverage, whiteness, gloss and adhesion (QURESHI, 2021).

The specific surface area of the granite waste was greater than that of the marble waste. A larger specific surface area is related to the smaller particle size (KARLSSON ET AL., 2019). As Rooney and Meldrum (2020) exemplified, the ivory black pigment contains grains with an approximate diameter of 10 μm, presenting an approximate specific surface area of 0.3 m^2/g. In comparison, the white titanium pigment has grains of approximately 0.5 μm in diameter and an approximate specific surface area of 3 m^2/g. This is one of the factors that directly influence the interaction between pigments and their surroundings (SARKODIE ET AL., 2019). As particle size decreases, an increase in specific surface area is expected, resulting in greater resin consumption to coat the pigments (LOPES ET AL., 2019; TOUAZI ET AL., 2020).

The organic matter content of the wastes is lower than 1%, which can be considered insignificant. When this content is high, it can cause damage to paints exposed to solar radiation and, in particular, to its UV components, in addition to the possible attack of fungi and bacteria (ROSSI; SIMEONI; QUARANTA, 2021; TRESSMANN et al., 2020).

Granite and marble waste had an alkaline pH ($pH > 7$), as in the case of several inert pigments used in paint production, such as calcium carbonate and hydrated alumina. According to Fadhil, Nashaan and Hlihl (2020), the pH of the pigment significantly affects the performance properties of the paints, and the recommended pH is between 8 and 9. In the production of paints, an alkaline pH can mitigate the proliferation of microorganisms and enhance adhesion to the cementitious substrate, which also exhibits an alkaline pH, consequently influencing the ultimate durability of the paint film (FAZENDA, 2009; SUMRA; PAYAM; ZAINAH, 2020). Nevertheless, research by Suma, Jacob and Joseph (2009) and Oliveira, Silva and Guerrini (2011) reveals that under alkaline conditions, polyvinyl acetate resin (PVA) can exhibit diminished hydrolytic stability, resulting in a decline in the reactivity index of the binder. According to Yamak (2013), the optimal pH range for polyvinyl acetate emulsions lies between 4.5 and 5.5.

The results of X-ray fluorescence (XRF) analyses are presented in Tables 1.3 and 1.4. The granite waste (Table 1.3) is mainly composed of SiO_2 and Al_2O_3, while the marble waste (Table 1.4) is mainly formed of CaO and MgO.

The results of mineralogical characterization based on X-ray diffraction (XRD) of the pigments are shown in Figure 1.3. The granite waste (Figure 1.3a) presented high-intensity peaks of quartz (SiO_2) and albite ($NaAlSi_3O_8$) and low-intensity signatures of muscovite ($KAl_2Si_3AlO_{10}(OH,F)_2$) and microcline ($KAlSi_3O_8$), while the marble waste (Figure 1.3b) presents strong peaks of calcite ($CaCO_3$) and dolomite ($CaMg(CO_3)_2$) and low-intensity peaks of quartz and muscovite. Several previous studies have already used these compounds in the formulation of paints (AHMED; MOHAMED; ABD EL-GAWAD, 2019; AL-KAYIEM et al., 2021; KOMAR et al., 2020; MOHAN; BHANUPRAKASH; MUKHERJEE, 2022; LE et al., 2021).

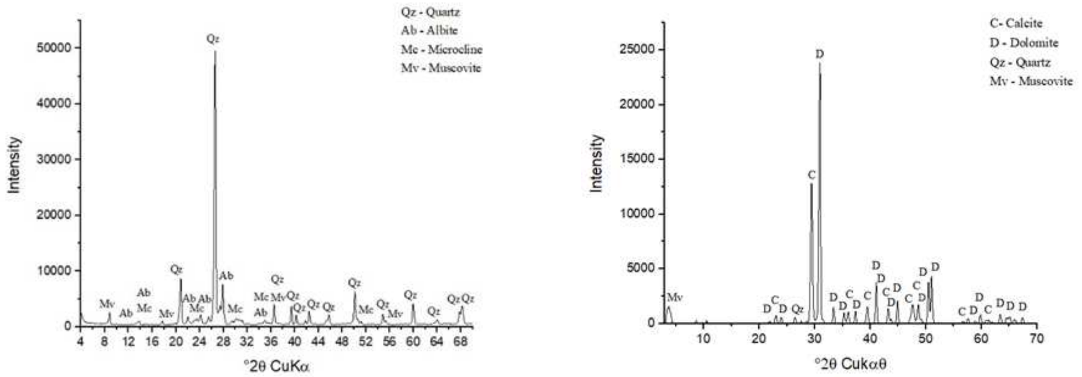
Table 1.3- Results of XRF analysis of granite waste pigments.

Pigment	SiO_2	Al_2O_3	Na_2O	K_2O	CaO	SO_3	Fe_2O_3	P_2O_5	Others
Granite waste	80.53	8.20	6.25	2.79	0.98	0.54	0.32	0.24	0.47

Table 1.4- Results of XRF analysis of marble waste pigments.

Pigment	CaO	MgO	SiO_2	K_2O	SO_3	Others
Marble waste	76.59	16.68	4.91	1.02	0.77	0.03

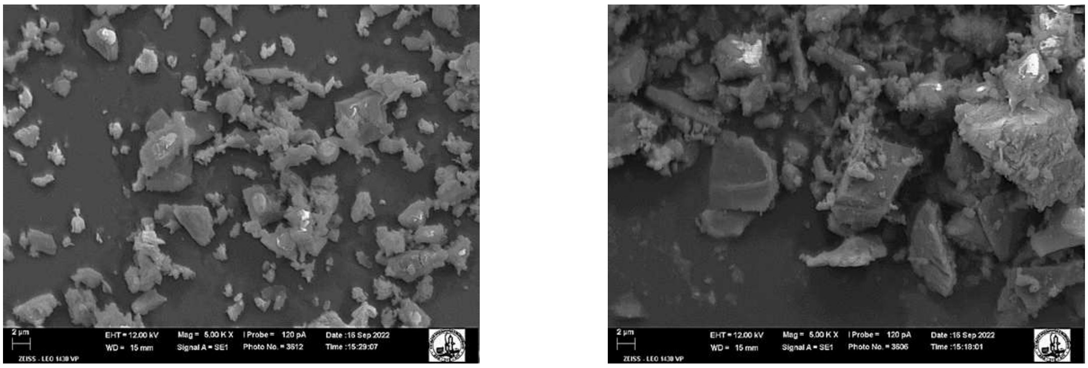
Figure 1.3- Result of the XRD analysis: (a) granite waste pigment; (b) marble waste pigment.



(a) (b)

Figures 1.4a and 1.4b show the morphological aspects of the granite waste and marble waste particles, respectively. The shape of the particles affects their packing conditions and, consequently, the hiding power of the paint film. Granite and marble wastes presented varied diameters, being composed of particles with irregular morphology and angular edges. This morphology is due to the ornamental stone processing process (SINGH; NAGAR; AGRAWAL, 2016). In addition to the shape of the particles, the SEM images show that the marble waste has larger particles compared to the granite waste. This variation in particle dimensions poses a challenge when comparing these residues. Instead of using a grinding treatment to standardize the grain size of the wastes, the current study exclusively concentrated on applying particles dispersion and sieving methods, as described in the “Pre-treatment of granite and marble wastes” section.

Figure 1.4- SEM of the particles: (a) granite waste pigment; (b) marble waste pigment (Mag.= 5000 X).



(a) (b)

3.2. Characterization and performance of paints

Table 1.5 presents the results of the different properties of the paints: specific gravity (SG), solids content (SC), pH, kinematic viscosity (KV), apparent viscosity (AV), plastic viscosity (PV), abrasion resistance (AR), hiding power (HP), in addition to the desirability (D) results obtained from the statistical analysis.

Table 1.5- Characteristics and properties of the paints.

Sample	SM (g/l)	SC (%)	pH	KV (s)	AV (cP)	PV (cP)	AR (cycles)	HP (m²/l)	D
GW55.0%	1336.70	59.00	7.30	19.00	84.00	77.00	40.00	14.20	0.63
GW50.0%	1468.20	55.50	7.40	17.00	65.50	60.00	49.00	10.50	0.70
GW47.5%	1353.30	56.10	7.40	19.00	70.50	69.00	115.00	4.60	1.00
GW45.0%	1419.90	50.50	7.40	14.40	28.50	35.00	64.00	6.20	0.80
GW42.5%	1183.90	50.80	7.40	16.50	41.00	42.00	69.50	4.30	0.83
GW40.0%	1243.00	52.20	7.30	20.70	68.50	60.00	143.00	3.30	0.91
GW37.5%	1335.00	46.20	7.30	14.10	25.00	28.00	107.50	3.60	0.95
GW35.0%	1318.60	47.00	7.30	17.20	43.00	39.00	127.00	3.20	0.89
GW30.0%	1270.40	42.00	7.20	14.30	24.50	22.00	160.00	2.10	0.72
MW55.0%	1353.90	60.50	7.60	17.10	52.00	52.00	23.00	7.30	0.48
MW50.0%	1343.80	56.20	7.60	14.00	42.50	38.00	28.00	6.50	0.53
MW47.5%	1591.40	57.10	7.50	17.50	60.50	48.00	80.00	5.50	0.89
MW45.0%	1374.70	50.70	7.50	12.80	31.50	20.00	40.00	5.40	0.63
MW42.5%	1439.40	52.10	7.50	15.80	50.50	31.00	94.00	3.60	0.92
MW40.0%	1393.60	53.40	7.50	17.00	38.50	42.00	97.50	1.00	0.49
MW37.5%	1340.00	47.60	7.50	14.60	22.50	17.00	62.50	3.30	0.72
MW35.0%	1321.20	47.70	7.40	14.80	23.50	20.00	115.00	1.50	0.61
MW30.0%	1175.10	43.60	7.30	14.60	26.00	19.00	115.00	0.90	0.47
GW10.6%+MW38.1%	1203.10	55.30	7.60	16.70	46.00	42.00	72.00	4.60	0.85

GW10.6%+MW33.1%	1274.10	49.30	7.60	13.60	26.00	26.00	85.00	4.70	0.92
GW10.6%+MW30.6%	1220.70	51.60	7.50	16.60	34.50	36.00	132.00	3.30	0.91
GW10.6%+MW25.6%	1336.00	47.60	7.50	14.00	22.00	19.00	140.00	2.20	0.74
GW15.0%+MW15.0%	1272.20	42.00	7.40	14.10	20.50	18.00	170.00	1.50	0.61
GW17.5%+MW17.5%	1239.40	46.80	7.40	16.20	33.00	29.00	160.00	2.50	0.79
GW18.8%+MW18.8%	1256.90	45.80	7.40	13.30	17.50	16.00	115.00	3.90	0.99
GW20.0%+MW20.0%	1242.40	51.10	7.40	17.50	50.50	45.00	148.00	1.90	0.69
GW21.3%+MW21.3%	1169.60	50.80	7.50	16.90	35.00	38.00	112.00	3.00	0.87
GW22.5%+MW22.5%	1368.70	50.60	7.50	14.80	29.00	29.00	39.00	6.90	0.62
GW23.8%+MW23.8%	1360.90	55.60	7.60	17.60	55.00	56.00	110.00	4.30	1.00
GW25.0%+MW25.0%	1232.30	56.00	7.60	14.40	49.50	52.00	43.50	6.10	0.66
GW25.6%+MW10.6%	1309.60	45.50	7.40	14.30	22.50	25.00	142.50	2.80	0.84
GW27.5%+MW27.5%	1318.60	59.40	7.60	17.70	66.50	67.00	52.50	6.00	0.72
GW30.6%+MW10.6%	1315.90	50.60	7.40	18.40	44.50	42.00	143.00	2.80	0.84
GW33.1%+MW10.6%	1309.40	51.00	7.50	14.90	27.00	35.00	68.00	6.70	0.82
GW38.1%+MW10.6%	1346.40	54.60	7.50	18.80	51.00	53.00	65.00	5.40	0.81

Note 1 - SC: Solids Content; SG: Specific Gravity; KV: Kinematic Viscosity (represented by the flow time of the fluid in the viscometer Ford cup No. 4); AV: Apparent Viscosity; PV: Plastic Viscosity; AR: Abrasion Resistance; HP: Hiding Power; D: Desirability.
Note 2 - The lines highlighted in gray represent the paints produced only with granite waste, only with marble waste, and with both granite waste and marble waste that presented the best performance (higher desirability values).

Table 1.6 presents the polynomial models (regression equations) that describe the characteristics and performance properties of the paints. These models explain how each component affects the final behavior of the paint; whether there are any significant interactions between the components; whether the contribution of each component is positive or negative; and whether the behavior is linear or parabolic. In addition, the coefficient of determination (R^2) was presented. This coefficient indicates the fitness level of a generalized statistical model to the observed values of a random variable. Since all R^2 values are greater than 80%, it is possible to conclude that the developed models explain the data variance well.

Table 1.6- Valid polynomial models for the paints series with granite and marble waste pigments.

Regression Equations	**R^2**
SC= 97.28a + 99.61b + 3.69c + 45.06d	98.20%
pH = 7.05a + 7.46b + 7.66c + 5.01d + 1.79ab + 5.63ad + 5.44bd	87.62%
KV = 34.66a + 30.58b – 10.33c + 35.85d	85.26%
AV = 214.4a + 186.8b - 159.6c + 110.9d	82.24%
PV = 270.5a + 227.7b – 194.5c + 286.5d - 571.4ad - 544.6bd	96.12%
AR= - 51.79a – 98.20b + 29.49c + 614.09d +386.48ab	88.24%
HP= 20.71a + 16.07b + 1.95c – 20.88d – 23.39ab	81.81%

Note: a- Granite waste; b- Marble waste; c- Water; d- Resin.

Table 1.7 presents the characteristics and properties of commercial paints used for comparisons with the granite and marble waste paints. It is noteworthy that the kinematic viscosity was not determined. As commercial paints have low fluidity, possibly due to the presence of thickening additives, it was not possible to measure their viscosity using the Ford cup viscosimeter No. 4.

Table 1.7- Characteristics and properties of commercial paints.

Commercial Paint	SM (g/l)	SC (%)	pH	KV (s)	AV (cP)	PV (cP)	AR (cycles)	HP (m²/l)
A	1520.20	41.60	9.90	-	67.50	25.00	95.00	7.50
B	1391.80	43.30	10.60	-	105.00	43.00	28.00	6.90
C	1311.20	38.00	10.00	-	55.00	28.00	52.00	4.80
D	1232.10	32.80	7.80	-	65.00	42.00	26.00	8.50
E	1530.30	54.30	9.30	-	95.50	40.00	38.00	10.10
F	1260.60	35.80	9.00	-	77.50	31.00	155.00	7.60
G	1416.00	44.60	9.90	-	84.00	16.00	264.00	10.60
H	1278.80	35.90	8.80	-	112.00	17.00	290.00	11.10

Note 1 - SC: Solids Content; SM: Specific Gravity; KV: Kinematic Viscosity; AV: Apparent Viscosity; PV: Plastic Viscosity; AR: Abrasion Resistance; HP: Hiding Power.

Note 2 - The lines highlighted in gray indicate the commercial paints that presented the best performances.

The specific gravity of the paints produced in this research ranged from 1169.6 g/L to 1591.4 g/L, compatible with the variation range found in commercial paints (1232.1 - 1530.3 g/L).

The solids content of the paints prepared in the present paper ranged from 42 to 60.5%. It is observed that commercial paints have a lower solids content, ranging from 32.8 to 54.3%. According to Lopes et al. (2019), a higher solids content provides greater opacity to paints. Furthermore, a higher solids content indicates greater waste consumption in the case of paints produced with granite and marble waste, i.e., the paint is more environmentally friendly. The regression equation generated for this parameter indicates that the granite and marble wastes have a similar contribution and that the water has an almost null contribution compared to the other parameters.

The pH of paints containing only granite waste ranged from 7.1 to 7.4. The paints produced only with marble waste had a pH in the range of 7.3 to 7.7. In addition, the paints produced with the two types of waste ranged from 7.4 to 7.7. These results are related to the pH values of the components used in the mixtures and their quantities: granite waste (pH = 8.89), marble waste (pH = 9.52), water (pH = 6.70), PVA resin (pH = 4.50). One can notice that the solution contains an excess of OH^- ions, indicating the occurrence of chemical reactions between the pigments and other paint components. According to the regression equation, significant interactions exist between the wastes and between the wastes and the resin, indicating a parabolic behavior of these components. Moreover, commercial paints have a higher pH, ranging from 7.8 to 10.6, due to the use of acrylic emulsion as resin, which has a pH in the range of 8.5 to 10.0. It is important to highlight that the main substrates used to apply real estate paints are cementitious materials with an alkaline pH. Therefore, if the paint has a lower pH, the substrate must receive a sealer or correction base to improve the adhesion of the paint, avoiding pathologies and increasing the durability of the finish (FAZENDA, 2009).

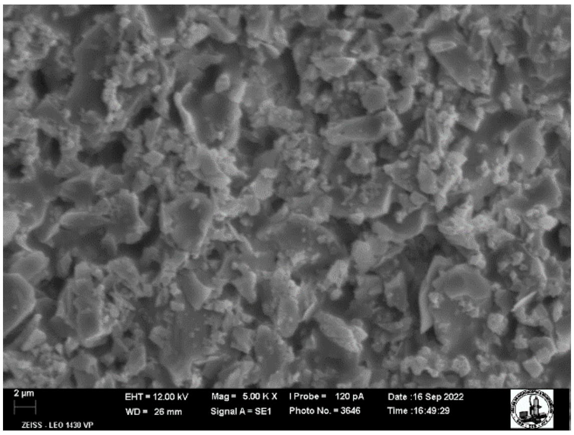
In general, viscosity results from cohesion between fluid molecules, with kinematic (KV), apparent (AV) and plastic viscosity (PV) being measured. KV is a gravity-based measure; AV is measured at a single point, keeping shear constant; VP is a measure of the friction resulting from the collision between the particles. The results described by the regression equations revealed that water is the only component that contributes negatively to viscosity because the greater the amount of water, the lower the viscosity of the fluid. The highest viscosity values were observed for the paints with the addition of granite waste. The differences in viscosity caused by the type of pigment are due to their different morphological and physical characteristics, such as size, particle size distribution and specific surface area. Smaller particles with a higher specific surface area have a greater number of particle-particle interactions and an increase in flow resistance, leading to increased viscosity. This result was also observed by Wołosiak-Hnat et al. (2019) when comparing paints with additions of different pigments (TiO_2, ZnO, $BaSO_4$). It is important to emphasize that pigments have different chemical compositions. Therefore, another factor that can influence viscosity is the interaction of the resin with the pigments. In this sense, a significant negative interaction between the waste particles and the resin was observed only in the case of PV, indicating a parabolic behavior of these components. The results also proved that increasing the amount of PVA resin considerably increases the viscosity. In terms of comparisons with commercial paints, it is observed that the AV (17 to 84 cP) and PV (16 to 77 cP) of granite and marble waste paints presented ranges of variation in common with the AV (55 to 112 cP) and the PV (16 to 43 cP) of commercial paints. The differences in viscosity values may be attributed to the reduced size of the pigment particles used in commercial paints. It is important to emphasize that the viscosity of the paint affect the application of the product, the coverage, the visual aspect, the durability, and the resistance of the dry paint film. Therefore, the amount of solvent present in the paints was controlled (BILGIN et al., 2022; FAZENDA, 2009).

Abrasion resistance is especially affected by the amount of resin in the mixture. When formulating paints, it is necessary to add enough resin content to envelop the pigment particles and allow the paint to adhere properly to the desired surface (SARKODIE et al., 2019). With the results obtained evidenced that the resin variation range used in the experimental program is quite comprehensive. This allows for the production of paints with varying degrees of abrasion resistance, ranging from very low (indicative of low resin consumption) to higher levels (indicative of high resin consumption), which are compatible with the values required by NBR15079-1 (ABNT, 2019b). Figure 1.5 presents electron microscope images of paints produced only with granite waste and paints produced only with marble waste. The paints with the highest amount of waste and those with the highest amount of resin were selected for these microscopic analyses. In Figures 1.5a and 1.5c, it is possible to observe a low resin content compared to the amount of pigments, resulting in low abrasion resistance. The smaller the amount of resin, the rougher the paint film, the greater the friction with the brush and the lower the abrasion resistance. In contrast, Figures 1.5b and 1.5d show an excess of resin associated with materials with high abrasion resistance. In Figure 1.5b, excess resin and a smoother surface are observed due to the smaller particle size of the granite residue, which guarantees fewer empty spaces between the grains and concentration of excess resin on the surface. In Figure 1.5d, there is also an excess of resin, but with a rougher surface due to the presence of larger particles and more spaces between them, which are being filled by the resin. Therefore, the excess resin is not entirely concentrated on the surface.

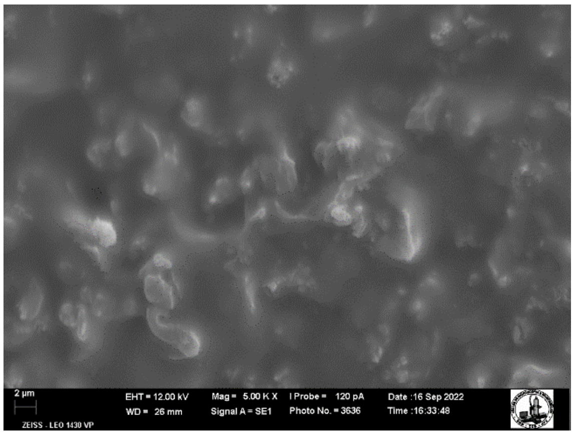
According to the regression equation, the wastes contribute negatively to abrasion resistance, and the marble waste exhibited the most harmful effects on this parameter. Figure 1.5 shows that the paint films with marble waste had larger particles, which provided greater roughness to the paint. On the other hand, granite waste had a finer granulometry and was predominantly formed by SiO_2, which is often used in the paint industry to improve abrasion and scratch resistance and provide surface superhydrophobic abilities (AL-KATTAN et al., 2015; NGUYEN; NGUYEN; NGUYEN, 2020). Therefore, paints produced with granite waste had a higher abrasion resistance.

The paints produced only with granite waste presented abrasion resistance ranging from 40 to 160 cycles. The abrasion resistance of marble waste paints ranged from 23 to 115 cycles. Additionally, paints produced with both granite and marble waste had abrasion resistance between 39 and 170 cycles. Commercial paints present an abrasion resistance ranging from 26 to 290 cycles. Therefore, it is possible to observe that all waste paints presented abrasion resistance similar to those of paints available in the market, except for the MW55.0% sample, which presented an abrasion resistance of 23 cycles. Low abrasion resistance causes reduced durability of coatings, rapid surface degradation due to contact with abrasive materials, and a decrease in the substrate's lifespan (FAZENDA, 2009). Some commercial paints have better performance than the paints produced in this study. It happens because the paint industry generally works with pigments with particle sizes between 0.1 and 10 µm (SARKODIE et al., 2019), depending on the paint type and use. Moreover, acrylic resins and various additives are used in those materials, impacting production costs and the environment.

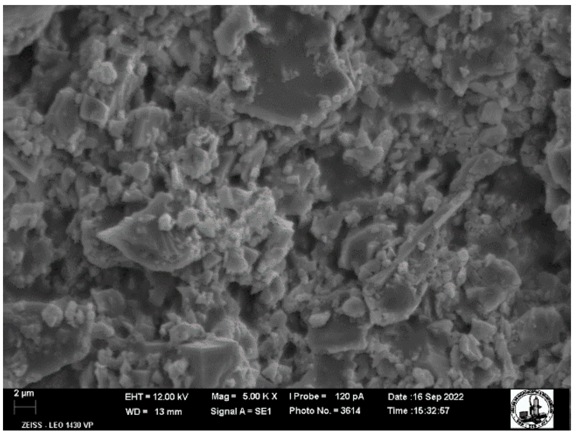
Figure 1.5- SEM of the paint films: (a) GW55%; (b) GW30%; (c) MW55%; (d) MW30% (Mag.= 5000X).



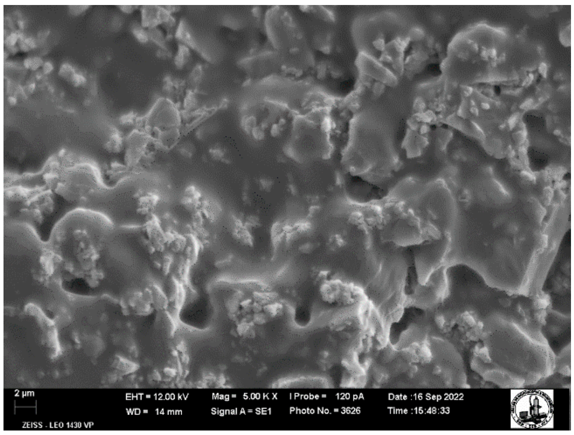
(a)



(b)



(c)



(d)

Regarding the hiding power, the regression equations indicate that the higher the percentage of pigments, the greater the paint coverage. In addition, paints produced with granite waste showed better hiding power than paints with marble waste. Pigment particle size is a critical parameter that affects surface finishing. According to Sarkodie et al. (2019), the tendency for a pigment to have good hiding power is also related to its good light-absorbing or -scattering properties. Fine particles produce a uniform surface because the angle of incident light is close to the angle of reflected light.

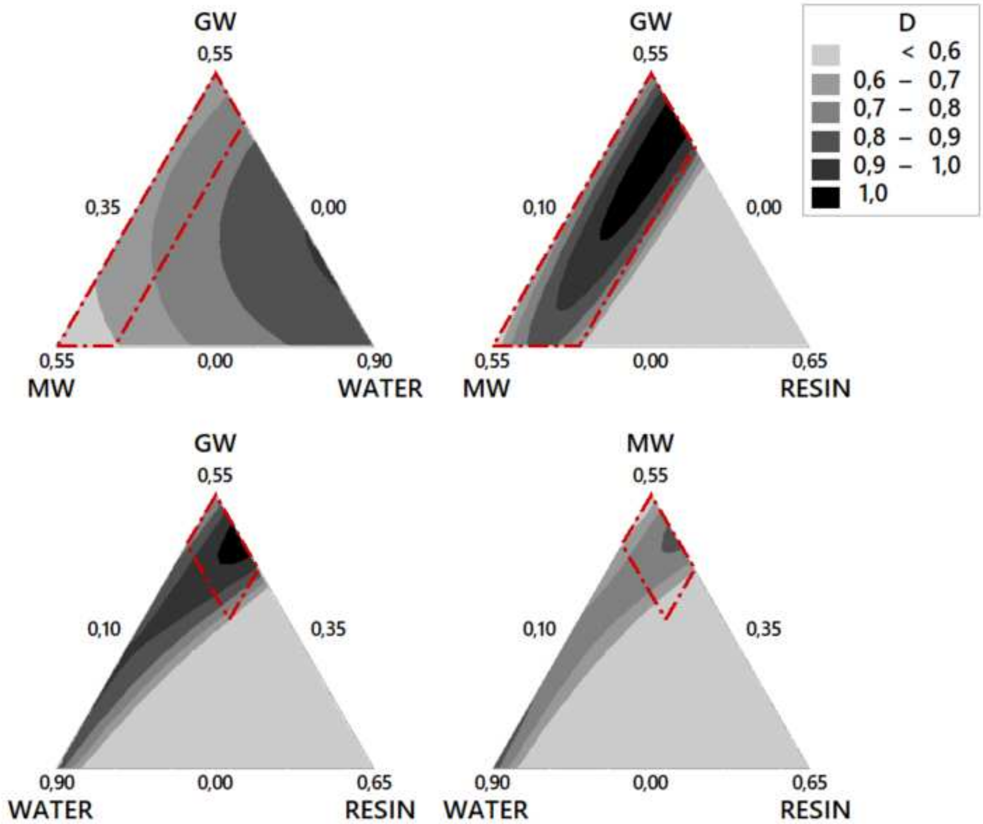
The paints produced only with granite waste presented hiding power ranging from 2.10 to 14.20 m^2/L. The hiding power of marble waste paints ranged from 0.90 to 7.30 m^2/L. Additionally, paints containing both granite and marble wastes had hiding power ranging between 1.50 and 6.90 m^2/L. Comparing these values with those verified in commercial paints (ranging from 4.80 to 11.10 m^2/L), it is possible to observe that several paints produced in this study presented hiding power values lower than the minimum value verified in commercial paints. In fact, the paint industry generally works with fine pigments down to the nanometer scale, high refractive index, various additives and chemical treatments/reagents to produce modified pigments for satisfactory applications (SARKODIE et al., 2019).It is crucial to highlight that low hiding power leads to inadequate coverage, increased product consumption to cover the substrate (requiring more layers), and reduced product yield (FAZENDA, 2009).

It is important to note that abrasion resistance and hiding power are antagonistic properties. In the regression equations, it is possible to observe that the components that contribute positively to the hiding power have an opposite effect on abrasion resistance. Thus, it is necessary to determine the contents of each material that would provide satisfactory performance for the paint.

Figure 1.6 shows the response surface generated for the statistical desirability function (D). The red line highlights the region studied in this work. In some regions, it is possible to obtain desirability values equal to 1, meaning that there are paint samples with a hiding power greater than 4 m^2/L and abrasion resistance greater than 100 cycles. These paints perform satisfactorily according to the economical category NBR15079-1 (ABNT, 2019b). The paints with the best performances are those composed of 0.41-0.47 GW, 0.35 water and 0.18-0.24 PVA resin or 0.21-0.28 GW; 0.17-0.27MW; 0.35 water, 0.17-0.20 PVA resin. So, paints produced only with marble waste had less satisfactory performances.

Furthermore, the paints with the best performance had the lowest water contents used in this experimental design. However, it does not mean that water impairs the performance of paints. According to the regression equations, water contributes positively to abrasion resistance and hiding power. However, other components promote more significant performance gains. In addition, the paints composed of granite and marble waste required less resin to perform satisfactorily. This behavior can be attributed to the lower specific surface area of the marble waste particles, which would require a smaller amount of resin to cover the grains.

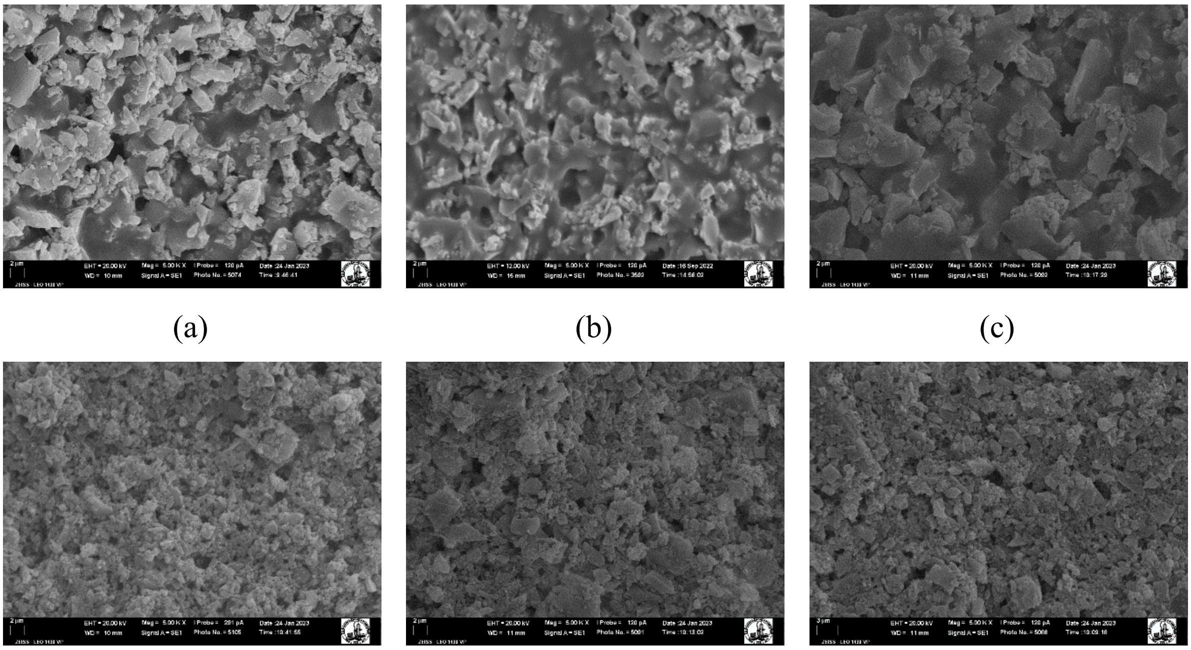
Figure 1.6- Response surface generated for the statistical desirability function (D).



Figures 1.7 and 1.8 show comparisons between experimental analyses of samples of the commercial paints with the best performances (F, G and H) and granite waste and/or marble waste paints with the best performances (GW47.5%, MW42.5% and GW23.8%+MW23.8%). The SEM images indicated that commercial paints have a greater number of small pigment particles. However, it is also possible to identify larger particles, probably the mineral fillers used in industrial paints. Furthermore, an excess of resin cannot be seen in SEM images of commercial paints. In contrast, Figures 1.7a, 1.7b, and 1.7c show some regions of high resin concentration, which may even indicate a non-uniform distribution of the binder in the paint film.

The profilometry images of the paint films illustrate that the smallest pigment particles promote less roughness (RG) to the film, which impacts the resistance to scratching and abrasion. According to Figure 1.8, the roughness of waste paints is more than 200% higher than the roughness of commercial paints.

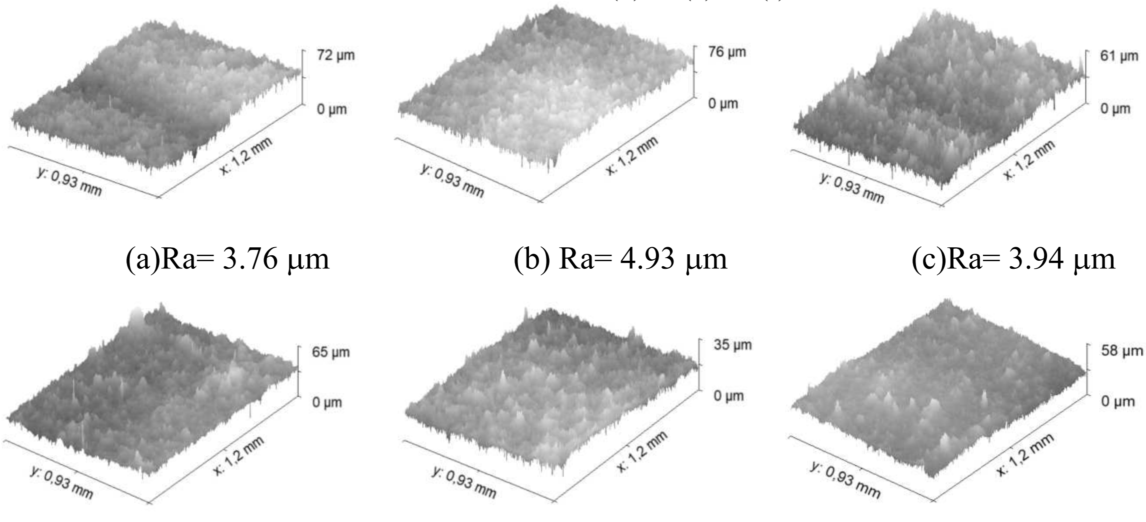
Figure 1.7- SEM of paint films: (a) GW47.5%; (b) MW42.5%; (c) GW23.8%+MW23.8%; (d) F; (e) G; (f) H.



(a) (b) (c)

(d) (e) (f)

Figure 1.8- Profilometry of paint films: SEM of paint films: (a) GW47.5%; (b) MW42.5%; (c) GW23.8%+MW23.8%; (d) F; (e) G; (f) H.



(a)Ra= 3.76 µm (b) Ra= 4.93 µm (c)Ra= 3.94 µm

(d) Ra= 2.69 µm (e) Ra= 2.38 µm (f) Ra= 1.77 µm

4. CONCLUSION

This study aimed to optimize the composition of paints produced using waste materials from ornamental stone processing by employing a quaternary mixture design, with the goal of achieving performance compatible with technical standards and commercial paints. The following conclusions were drawn from the results of the experimental tests:

- the experimental design of mixtures composed of four components (granite waste, marble waste, water, and PVA resin) allowed for the development of polynomial models that described the characteristics and properties of the paints;
- although a special cubic model with fourth-order terms was utilized, most of the polynomial models exhibited linear behavior, indicating that the interactions between the components were not statistically significant;
- paints formulated with granite waste demonstrated superior hiding power and abrasion resistance compared to those produced with marble waste. This can be attributed to the smaller particle size and favorable chemical composition of granite waste for paint formulation;
- the hiding power was positively influenced by the type and amount of pigment in the mixture, while the resin content positively affected abrasion resistance;
- the optimal paint formulations consisted of 41-47% granite waste, 35% water, and 18-24% PVA resin, or alternatively, 21-28% granite waste, 17-27% marble waste, 35% water, and 17-20% PVA resin. These formulations met the minimum requirements for hiding power and abrasion resistance set by the technical standards for the economic paint category; and
- the optimal paints developed in this study exhibited similar values of solids content, hiding power, and abrasion resistance compared to commercial paints. However, it is important to note that the granite and marble waste paints did not contain additives, acrylic resin, or undergo complex pigment treatments. Consequently, the paints developed in this research offer environmentally friendly alternatives.

Overall, this study demonstrates the potential of utilizing waste materials from ornamental stone processing to produce paints with satisfactory performance and reduced environmental impact. The optimized formulations can contribute to the development of sustainable paint solutions that align with technical standards and offer economic advantages. It is important to emphasize that further complementary studies are needed to assess the durability of these paints. Additionally, efforts should be made to explore the use of additives to enhance the performance (abrasion resistance and hiding power) and durability of the developed product. Future research is also strongly recommended to investigate the effects of different types of waste grinding treatments (variations in grinding equipment, duration, speed, etc.) to further understand their impact on the performance of the sustainable paints. Cost-effectiveness assessments of paint production should also be conducted to express the economic viability of the product.

REFERENCES

AHMED, N. M.; MOHAMED, M. G.; MABROUK, M. R.; ELSHAMI, A. A. Novel anticorrosive pigments based on waste material for corrosion protection of reinforced concrete steel. **Construction and Building Materials**, v. 98, p. 388–396, 2015.

AHMED, N. M.; MOHAMED, M. G.; ABD EL-GAWAD, W. M. The assessment of anticorrosive behavior of calcium carbonate from different sources in alkyd-based paints. **Progress in Organic Coatings**, v. 128, p. 168–180, 2019.

ALAM, M.; ALANDIS, N. M. Development of ambient cured polyesteramide coatings from linseed oil: a sustainable resource. **Journal of Polymers and the Environment**, v. 19, n. 2, p. 391–397, 2011.

AL-KATTAN, A.; WICHSER, A.; VONBANK, R.; BRUNNER, S.; ULRICH, A.; ZUIN, S.; ARROYO, Y.; GOLANSKI, L.; NOWACK, B. Characterization of materials released into water from paint containing nano-SiO2. **Chemosphere**, v. 119, p. 1314–1321, 2015.

AL-KAYIEM, H. H.; ISMAEEL, A. A.; BAHETA, A. T.; AURYBI, M. A. Performance enhancement of solar vortex power generator by Al2O3-in-black paint coating. **Journal of Cleaner Production**, v. 316, p. 128303, 2021.

ALMADA, B. S.; MELO, L. de S.; DUTRA, J. B.; BUBANI, L. C.; SILVA, G. J. B.; SANTOS, W. J. dos; AGUILAR, M. T. P. Influence of the heterogeneity of waste from wet processing of ornamental stones on the performance of Portland cement composites. **Construction and Building Materials**, v. 262, p. 120036, 2020.

ALMEIDA, K. M. de; GADIOLI, M. C. B.; SAGRILLO, V. P. D.; DE AGUIAR, M. C. Industrial Scale Manufacturing of Red Ceramic Sealing Blocks with Ornamental Stone Wastes. **Revista de Gestão Social e Ambiental**, vol. 17, nº 10, p. e04141, 11 out. 2023. https://doi.org/10.24857/rgsa.v17n10-015.

AMERICAN SOCIETY FOR TESTING AND MATERIALS. **D 2805-11**: standard test method for hiding power of paints by reflectometry. West Conshohocken, PA, 2018.

AMERICAN SOCIETY FOR TESTING AND MATERIALS. **D 3723-05**: standard test method for pigment content of water-emulsion paints by low-temperature ashing. West Conshohocken, PA, 2017.

AMERICAN SOCIETY FOR TESTING AND MATERIALS. **D 4060-19**: standard test method for abrasion resistance of organic coatings by the taber abraser. West Conshohocken, PA, 2019.

ANIYIKAIYE, T.; OLUSEYI, T.; ODIYO, J.; EDOKPAYI, J. Physico-chemical analysis of wastewater discharge from selected paint industries in Lagos, Nigeria. **International Journal of Environmental Research and Public Health**, v. 16, n. 7, p. 1235, 2019.

ASSOCIAÇÃO BRASILEIRA DA INDÚSTRIA DE ROCHAS ORNAMENTAIS (ABIROCHAS). **Balanço das exportações e importações de rochas no 1º trimestre de 2023**. 2023 Available: https://abirochas.com.br/noticias/balanco-das-exportacoes-e-importacoes-de-rochas-no-1o-trimestre-de-2023/#:~:text=jun-,BALAN%C3%87O%20DAS%20EXPORTA%C3%87%C3%95ES%20E%20IMPORTA%C3%87%C3%95ES%20DE%20ROCHAS%20NO%201%C2%BA%20TRIMESTRE,e%20364%2C3%20mil%20toneladas. Access: August 2023.

ASSOCIAÇÃO BRASILEIRA DE NORMAS TÉCNICAS. **NBR 13600:** Solo - Determinação do teor de matéria orgânica por queima a 440 °C. Rio de Janeiro, 2022.

ASSOCIAÇÃO BRASILEIRA DE NORMAS TÉCNICAS. **NBR 14942:** Tintas para construção civil - Método para avaliação de desempenho de tintas para edificações não industriais - Determinação do poder de cobertura de tinta seca e rendimento teórico. Rio de Janeiro, 2019a.

ASSOCIAÇÃO BRASILEIRA DE NORMAS TÉCNICAS. **NBR 15078:** Tintas para construção civil - Método para avaliação de desempenho de tintas para edificações não industriais - Determinação da resistência à abrasão úmida sem pasta abrasiva. Rio de Janeiro, 2006.

ASSOCIAÇÃO BRASILEIRA DE NORMAS TÉCNICAS. **NBR 15079-1:** Tintas para construção civil — Requisitos mínimos de desempenho - Parte 1: Tinta látex fosca nas cores claras. Rio de Janeiro, 2019b.

ASSOCIAÇÃO BRASILEIRA DE NORMAS TÉCNICAS. **NBR 16605:** Cimento Portland e outros materiais em pó — Determinação da massa específica. Rio de Janeiro, 2017.

ASSOCIAÇÃO BRASILEIRA DE NORMAS TÉCNICAS. **NBR 5849:** Tintas — Determinação de viscosidade pelo copo Ford. Rio de Janeiro, 2015.

ASSOCIAÇÃO BRASILEIRA DOS FABRICANTES DE TINTAS (ABRAFATI). **O setor de tintas no Brasil**. 2022. Available: https://abrafati.com.br/setor-de-tintas/dados-do-setor/. Access: August 2023.

BACARJI, E.; TOLEDO FILHO, R. D.; KOENDERS, E. A. B.; FIGUEIREDO, E. P.; LOPES, J. L. M. P. Sustainability perspective of marble and granite residues as concrete fillers. **Construction and Building Materials**, v. 45, p. 1–10, 2013.

BAL, K.; ÜNLÜ, K. C.; ACAR, I.; GÜÇLÜ, G. Epoxy-based paints from glycolysis products of postconsumer PET bottles: synthesis, wet paint properties and film properties. **Journal of Coatings Technology and Research**, v. 14, n. 3, p. 747–753, 2017.

BILGIN, S.; BAHRAEIAN, S.; LIEW, M. L.; TOMOVSKA, R.; ASUA, J. M. Surfactant-free latexes as binders in paint applications. **Progress in Organic Coatings**, v. 162, p. 106591, 2022.

BOZORG, M.; RAMEZANI, A. Characterization and protective performance of acrylic-based nanocomposite coating reinforced with silica nanoparticles. **Materials and Corrosion**, v. 68, n. 7, p. 725–730, 2017.

CARDOSO, F. de P.; ALVARENGA, R. de C. S. S.; CARVALHO, A. F. de; FONTES, M. P. F. Processos de produção e avaliação de requisitos de desempenho de tintas para a construção civil com pigmentos de solos. **Ambiente Construído**, Porto Alegre, v. 16, n. 4, p. 167–183, out./dez. 2016.

DIEBOLD, M.; BACKER, S. de; NIEDENZU, P. M.; HESTER, B. R.; VANHECKE, F. A. C. Extender Particles. **Pigments, Extenders, and Particles in Surface Coatings and Plastics**. Cham: Springer International Publishing, p. 319–356, 2022.

EMPRESA BRASILEIRA DE PESQUISA AGROPECUÁRIA (EMBRAPA). **Manual de Métodos de Análise de Solo**. 3. ed. Brasília, DF, 2017.

FADHIL, H. S.; NASHAAN, S. A.; HLIHL, B. H. Evaluation the influence of pH and temperature on the manufacturing process of latex paint. **AIP Conference Proceedings**, v. 2213, Mar. 2020.

FALLEH, H.; BEN JEMAA, M.; DJEBALI, K.; ABID, S.; SAADA, M.; KSOURI, R. Application of the mixture design for optimum antimicrobial activity: combined treatment of Syzygium aromaticum, Cinnamomum zeylanicum, Myrtus communis, and Lavandula stoechas essential oils against Escherichia coli. **Journal of Food Processing and Preservation**, v. 43, n. 12, 2019.

FAZENDA, J. M. R. **Tintas e vernizes: Ciência e tecnologia**. 4. ed. São Paulo: Edgard Blücher, 2009.

GALVÃO, J. L. B.; ANDRADE, H. D.; BRIGOLINI, G. J.; PEIXOTO, R. A. F.; MENDES, J. C. Reuse of iron ore tailings from tailings dams as pigment for sustainable paints. **Journal of Cleaner Production**, v. 200, p. 412–422, 2018.

GHANNAM, S.; NAJM, H.; VASCONEZ, R. Experimental study of concrete made with granite and iron powders as partial replacement of sand. **Sustainable Materials and Technologies**, v. 9, p. 1–9, 2016.

INTERNATIONAL ORGANIZATION FOR STANDARDIZATION (ISO). **ISO 10414-1**: Petroleum and natural gas industries — Field testing of drilling fluids — Part 1: Water-based fluids. Geneva, 2008.

KARLSSON, M. C. F.; ABBAS, Z.; BORDES, R.; CAO, Y.; LARSSON, A.; TAYLOR, P.; STEENARI, B. M. Characterisation of silicon, zirconium and aluminium coated titanium dioxide pigments recovered from paint waste. **Dyes and Pigments**, v. 162, p. 145–152, 2019.

KOMAR, V. V.; POCHODINA, T. A.; KULINICH, N. V.; KRUTKO, N. P.; OVSEENKO, L. V. Modification of water-suspension epoxy varnish and paint materials by nanostructured magnesium oxide. **Proceedings of the National Academy of Sciences of Belarus, Chemical Series**, v. 56, n. 1, p. 105–113, 2020.

LE, M.-C.; LE, T.-H.; BUI THI, T.-H.; NGUYEN, Q.-D.; DO THI, T.-H.; TRAN THI, M.-N.. Synthesizing and evaluating the photocatalytic and antibacterial ability of TiO2/SiO2 nanocomposite for silicate coating. **Frontiers in Chemistry**, v. 9, 2021.

LEGODI, M. A.; DE WAAL, D. The preparation of magnetite, goethite, hematite and maghemite of pigment quality from mill scale iron waste. **Dyes and Pigments**, v. 74, n. 1, p. 161–168, 2007.

LI, Z.; LU, D.; GAO, X. Optimization of mixture proportions by statistical experimental design using response surface method: a review. **Journal of Building Engineering**, v. 36, p. 102101, 2021.

LOPES, M. M. S.; PEDROTI, L. G.; DE LIMA, G. E. S.; RIBEIRO, J. C. L.; NALON, G. H.; MENDES, B. C.; DE OLIVEIRA, A. L. Influence of the incorporation of granite waste on the weathering resistance of soil pigment-based paints. **Characterization of Minerals, Metals, and Materials 2021**. Springer ed., p.471–481, 2021b. Available: https://link.springer.com/chapter/10.1007/978-3-030-65493-1_47 Access: August 2023.

LOPES, M. M. S.; PEDROTI, L. G.; DE OLIVEIRA, A. F.; RIBEIRO, J. C. L.; CARVALHO, J. M. F. de; CARVALHO, A. F. de; CARDOSO, F. de P.; NALON, G. H.; DE LIMA, G. E. S. Optimization of performance of sustainable paints using granite waste through the variation of particle size and pH. **Journal of Cleaner Production**, v. 326, p. 129418, 2021. 2021a.

LOPES, M. M. S.; ALVARENGA, R. de C. S. S.; PEDROTI, L. G.; RIBEIRO, J. C. L.; CARVALHO, A. F. de; CARDOSO, F. de P.; MENDES, B. C. Influence of the incorporation of granite waste on the hiding power and abrasion resistance of soil pigment-based paints. **Construction and Building Materials**, v. 205, p. 463–474, 2019.

MANDAL, J.; YANG, Y.; YU, N.; RAMAN, A. P. Paints as a scalable and effective radiative cooling technology for buildings. **Joule**, v. 4, n. 7, p. 1350–1356, 2020.

MOHAN, M. V. K.; BHANUPRAKASH, T. V. K.; MUKHERJEE, A. Al_2O_3 and CuO nano particulate-based paints for marine applications. **Engineering Research Express**, v. 4, n. 3, p. 035056, 2022.

MORDOR INTELLIGENCE. **Mercado tintas e revestimentos**: crescimento, tendências, impacto covid-19 e previsões (2022-2027). 2022. Available: https://www.mordorintelligence.com/pt/industry-reports/paints-and-coatings-market. Access: August 2023.

MORENO, M.; MIRANDA, J. I.; GOIKOETXEA, M.; BARANDIARAN, M. J. Sustainable polymer latexes based on linoleic acid for coatings applications. **Progress in Organic Coatings**, v. 77, n. 11, p. 1709–1714, 2014.

MYINT, S.; ZAKARIA, M. S. B.; AHMED, K. R. Paints based on waste expanded polystyrene. **Progress in Rubber, Plastics and Recycling Technology**, v. 26, n. 1, p. 21–30, 2010.

NASCIMENTO, E. S. S.; SOUZA, P. C. de; OLIVEIRA, H. A. de; MELO JÚNIOR, C.. M.; ALMEIDA, V. G. de O.; MELO, F. M. C. de. Soil-cement brick with granite cutting residue reuse. **Journal of Cleaner Production**, v. 321, p. 129002, 2021.

NGUYEN, T. V.; NGUYEN, T. A.; NGUYEN, T. H. The Synergistic Effects of Sio2 Nanoparticles and Organic Photostabilizers for Enhanced Weathering Resistance of Acrylic Polyurethane Coating. **Journal of Composites Science**, v. 4, n. 1, p. 23, 2020.

NOVAES, C. G.; YAMAKI, R. T; DE PAULA, V. F. Optimization of analytical methods using response surface methodology: part II: mixture variables. **Revista Virtual de Química**, p. 393–420, 2018.

OLIVEIRA, M. P. de; SILVA, C. R.; GUERRINI, L. M. Effect of itaconic acid on the wet scrub resistance of highly pigmented paints for architectural coatings. **Journal of Coatings Technology and Research**, v. 8, n. 4, p. 439–447, 2011.

ONG, H. C.; MILANO, J.; SILITONGA, A. S.; HASSAN, M. H.; SHAMSUDDIN, A. H.; WANG, C.-T.; INDRA MAHLIA, T. M.; SISWANTORO, J.; KUSUMO, F.; SUTRISNO, J. Biodiesel production from Calophyllum inophyllum-Ceiba pentandra oil mixture: Optimization and characterization. **Journal of Cleaner Production**, v. 219, p. 183–198, 2019.

OU, R.; CHANG, C.; ZENG, Y.; ZHANG, X.; FU, M.; FAN, L.; CHEN, P.; YE, D. Emission characteristics and ozone formation potentials of VOCs from ultra-low-emission waterborne automotive painting. **Chemosphere**, v. 305, p. 135469, 2022.

QURESHI, E. S. A. Effect of operating parameters and particle size of calcium carbonate on the physical properties of latex paint. **Biomedical Journal of Scientific & Technical Research**, v. 39, n. 1, p. 30909–30915, 2021.

ROONEY, M.; MELDRUM, T. Effect of pigment concentration on NMR relaxometry in acrylic paints. **Magnetic Resonance in Chemistry**, v. 58, n. 9, p. 880–888, Sep. 2020.

ROSSI, S.; SIMEONI, M.; QUARANTA, A. Behavior of chromogenic pigments and influence of binder in organic smart coatings. **Dyes and Pigments**, v. 184, n. September 2020, p. 108879, 2021.

SARKODIE, B.; ACHEAMPONG, C.; ASINYO, B.; ZHANG, X.; TAWIAH, B. Characteristics of pigments, modification, and their functionalities. **Color Research & Application**, v. 44, n. 3, p. 396–410, 2019.

SAXENA, M.; DHIMOLE, L. Utilization and value addition of copper tailing as an extender for development of paints. **Journal of Hazardous Materials**, v. 129, n. 1–3, p. 50–57, 2006.

SILVA, I. L. M. **Estudo de durabilidade de pinturas "frias" e convencionais expostas ao envelhecimento natural**. Universidade de São Paulo, São Paulo, 2017.

SILVA, J. M. da; UEMOTO, K. L. **Caracterização de tintas látex para construção civil**: diagnóstico do mercado do estado de São Paulo. Available: http://dx.doi.org/10.1016/j.cirp.2016.06.001%0Ahttp://dx.doi.org/10.1016/j.powtec.2016.12.055%0Ahttps://doi.org/10.1016/j.ijfatigue.2019.02.006%0Ahttps://doi.org/10.1016/j.matlet.2019.04.024%0Ahttps://doi.org/10.1016/j.matlet.2019.127252%0Ahttp://dx.doi.o. Access: August 2023.

SINGH, S.; NAGAR, R.; AGRAWAL, V. Performance of granite cutting waste concrete under adverse exposure conditions. **Journal of Cleaner Production**, v. 127, p. 172–182, 2016.

SOUZA, L. G. M.; SANTOS, N. R.; CAVALCANTE, A. G.; SOUZA, L. G. V. M.; COSTA, L. C. F. Composite utilizing residues of marble and granite for building popular homes. **Journal of Building Engineering**, v. 9, p. 192–197, 2017.

SUMA, K. K.; JACOB, S.; JOSEPH, R. Paint formulation using water based binder and property studies. **Macromolecular Symposia**, v. 277, n. 1, p. 144–151, 2009.

SUMRA, Y.; PAYAM, S.; ZAINAH, I. The pH of cement-based materials: a review. **Journal of Wuhan University of Technology- Materials Science Edition,** v. 35, n. 5, p. 908–924, 2020.

SYAFITRI, U.; SARTONO, B.; GOOS, P. I-optimal design of mixture experiments in the presence of ingredient availability constraints. **Journal of Quality Technology**, v. 47, n. 3, p. 220–234, 2015.

TOUAZI, Y.; ABDI, A.; LESHAF, A.; KHIMECHE, K.. Influence of heat treatment of iron oxide on its effectiveness as anticorrosion pigment in epoxy based coatings. **Progress in Organic Coatings**, v. 139, n. October, p. 105458, 2020.

TRESSMANN, D. M. G. A.; PEDROTI, L. G.; CARVALHO, A. F. de; RIBEIRO, J. C. L.; CARDOSO, F. de P.; LOPES, M. M. S; OLIVEIRA, A. F. de; FERREIRA, S. O. Research into the use of marble waste as mineral filler in soil pigment-based paints and as an active pigment in waterborne paints. **Construction and Building Materials**, v. 241, p. 117976, 2020.

WOŁOSIAK-HNAT, A.; ZYCH, K.; MĘŻYŃSKA, M.; KARŁOWICZ, M.; DAJWORSKI, M.; BARTKOWIAK, A.; LISIECKI, S. The influence of type and concentration of inorganic pigments on the polyurethane adhesive properties and adhesion of laminates. **International Journal of Adhesion and Adhesives**, v. 90, p. 1–8, 2019.

YAMAK, H. B. Emulsion Polymerization: effects of polymerization variables on the properties of vinyl acetate based emulsion polymers. **Polymer Science**. Publisher: INTECH, 2013.

ARTICLE 2.

IMPACT OF BIOCIDAL AND DISPERSANT ADDITIVES ON SUSTAINABLE PAINTS FOR CONSTRUCTION CONTAINING GRANITE AND MARBLE WASTE

ABSTRACT

The reuse of waste generated from granite and marble processing as inert pigments in eco-friendly paints shows promise. However, the lack of an effective process for dispersing and stabilizing pigments, along with the low resistance of mixtures to attack by biological agents, can compromise the performance or even make the use of these paints unfeasible. Therefore, this study aims to provide new insights into this area by investigating the effects of biocidal and dispersant additives on the performance of PVA latex paints made from granite and marble waste. Through an experimental mixture design, varying proportions of waste and additives were systematically investigated. Tests were conducted for determination of solid content, pH, viscosity, dispersion quality, resistance to bacterial growth, hiding power, and abrasion resistance. The results indicated that adding biocidal additives maintained paint properties and significantly reduced bacterial growth, extending shelf-life. However, the inclusion of dispersant additives improved the components dispersion, but compromised the paint abrasion resistance. Thus, caution is warranted when using high concentrations of dispersant additives. In summary, this study provided guidance for formulating sustainable and performance-effective paints.

Keywords: Additives. Granite waste. Marble waste. Paints. Performance.

1. INTRODUCTION

In recent decades, sustainable development has become a major challenge in the construction industry. Professionals from various fields are actively seeking solutions to minimize the environmental impact of construction projects, leading to numerous studies on this issue (FEI *et al.*, 2021; JOSIAH MARUT; ALAEZI; OBEKA, 2020). Research on incorporating waste into concrete, mortar, and ceramics has led to well-established findings and various applications (DANISH *et al.*, 2021; GOL *et al.*, 2022; KORE; VYAS; KABEER K.I., 2020; LI *et al.*, 2022; NASCIMENTO *et al.*, 2020; SANTOS NASCIMENTO *et al.*, 2021;

SINGH CHOUHAN *et al.*, 2019; SRIVASTAVA; SINGH, 2020; TUGRUL TUNC, 2019). However, studies on the reuse of waste for production of polymer materials, especially sustainable paints, still require more attention.

Previous works that developed paints with reduced environmental, social, and economic impacts (AZEVEDO, 2018; GALVÃO *et al.*, 2018; LOPES *et al.*, 2019; TRESSMANN *et al.*, 2020) have utilized waste from kaolin processing, iron ore tailings from tailing dams, waste from granite processing, and waste from marble processing as raw materials. Wastes from granite and marble processing consist mostly of rock fragments, suggesting that they can be used as inert pigments in paint production (LOPES *et al.*, 2021; MARRAS *et al.*, 2022). However, Lopes et al. (2019) highlighted the need for improved pigment preparation, based on the use of equipment that ensures better disaggregation and dispersion of waste particles in the mixture, as well as the utilization of additives that confer specific performance properties to the paints. Additionally, Tressmann et al. (2020) reported the appearance of fungi and bacteria in paints produced with marble waste, compromising the product's durability. Two-pigment paint systems offer the potential for precise adjustment of the paint's optical properties, striking a harmonious balance between the advantages and disadvantages inherent in each pigment (ATIGANYANUN; KUMNORKAEW, 2023).

The growth of microorganisms depends on various factors, including the type of diluent, the chemical composition of the binder, and the pigment's type and concentration. When microorganisms affect water-based paints, they can alter properties while the paints are in liquid form during storage and after their application to a surface. Liquid paints may experience viscosity loss, gas release, or changes in color or pH. Once dried, the paint film primarily undergoes aesthetic changes, in addition to issues like bubble formation, peeling, or complete degradation (DANKOVÁ; KALENDOVÁ; MACHOTOVÁ, 2020; OBIDI; OKEKUNJO, 2017). Consequently, there is considerable interest in developing coatings that prevent the growth of fungi, bacteria, and algae, a research topic that has garnered significant attention and is rapidly expanding (GUPTA *et al.*, 2021). According to Piemonte et al. (2017), selecting effective broad-spectrum biocides, along with implementing proper manufacturing processes and hygiene practices, can facilitate the production of paints without long-term microbiological issues.

In terms of dispersion issues in paints, Jacob et al. (2022) described various destabilization phenomena that can occur, including sedimentation, flocculation, and syneresis. These phenomena involve and impact the solid particles of the paint, which include both active and inert pigments. Therefore, dispersion mechanisms are influenced by the size and volume of the dispersed particles, the viscosity of the continuous phase, and the type and concentration of dispersing agents. Dispersing agents are important for improving stability when the particle size and volume fraction cannot be adjusted, and viscosity must remain within a certain range. These agents prevent pigment particles from flocculating, thus averting sedimentation during storage (KARAKAŞ; ÇELIK, 2018; LOKHANDE; JAGTAP, 2016a, b).

The primary objective of this study is to evaluate the impact of dispersant and biocide additives on the performance of PVA latex paints formulated with polyvinyl acetate (PVA) resin and pigments derived from waste generated from the processing of granite and marble. The significance of this investigation is underscored by recent scholarly endeavors focusing on the integration of granite and marble waste as inert pigments of environmentally sustainable paint formulations (LOPES et al., 2021a; LOPES et al., 2021b; LOPES et al., 2019; TRESSMANN et al., 2020). Given the emerging nature of this recycling strategy, this work aims to provide a novel perspective to this evolving area of research.

2. MATERIALS AND METHODS

2.1. Materials

The materials selected for this study include waste generated from granite and marble processing, utilized as pigments; water, used as the solvent; polyvinyl acetate (PVA) resin, serving as the binder; a dispersant additive; and a biocide additive.

The granite and marble waste underwent initial treatments to disaggregate particles and achieve mechanical dispersion in an aqueous medium, conducted separately for each material. This processes used a Cowles disk coupled with a mechanical agitator, operating at a speed of 1500 rpm for 30 minutes, following the methodology proposed by Cardoso et al. (2016). Subsequently, wet sieving was performed using a 400 mesh ASTM sieve with a 0.037 mm aperture.

The main characteristics of these residues are listed in Table 2.1. Moreover, X-ray Fluorescence (XRF) analyses were carried out in a Shimadzu Micro-EDX-1300 spectrometer of the Soil Laboratory (DPS/UFV), using high voltage (50 keV and 50 μA) and mapping 1200 points. These analyses revealed that the granite residue was primarily composed of SiO_2, while the marble residue was predominantly constituted of CaO, as delineated in Table 2.2.

Table 2.1- Characterization of granite and marble waste after initial treatment.

Pigment	Specific gravity [1] (g/cm³)	Specific area [2] (m²/g)	Average diameter [3] (μm)	Organic matter content [4] (%)	pH [5]
Granite waste	2.60	6.11	6.31	0.55	8.89
Marble waste	2.82	4.42	9.99	0.20	9.52

Notes: [1] Specific gravity determined using Le Chatelier's volumetric flask NBR 16605 (ABNT, 2017).

[2] Specific area measured by the BET method.

[3] Mean diameter obtained from the granulometric distribution curve (Bettersize laser granulometer).

[4] Organic matter content measured by burning at 440 ºC NBR 13600 (ABNT, 2022).

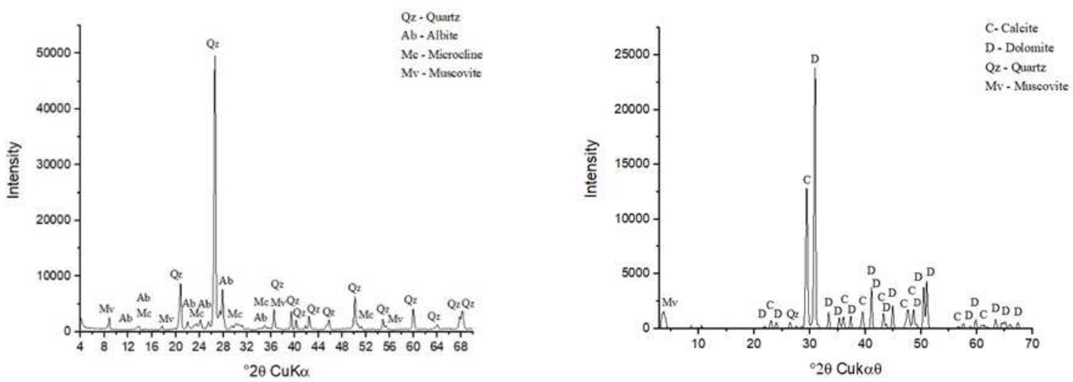
[5] pH determined using the methodology proposed by EMBRAPA (2017).

Table 2.2- XRF analysis of granite and marble waste pigments (percentages).

Pigment	SiO_2	Al_2O_3	K_2O	MgO	CaO	Na_2O	Fe_2O_3	SO_3	Others
Granite waste	84.62	8.60	2.67	1.29	1.00	0.94	0.41	-	0.47
Marble waste	4.91	-	1.02	16.68	76.59	-	-	0.77	0.03

The mineralogical characterization of the granite and marble waste was obtained through X-ray Diffraction (XRD) and illustrated in Figures 2.1a and 2.1b, respectively. XRD analyses were carried out in the Nanoscopy Laboratory (DPF/UFV) using the D8 Discover diffractometer (Bruker), CuKα radiation (1.5418 Å) and 2θ ranging from 3° to 70°. The XRD spectra show that the granite waste displays more prominent peaks of quartz (SiO_2) and albite ($NaAlSi_3O_8$), along with less intense peaks of muscovite ($KAl_2Si_3AlO_{10}(OH,F)_2$) and microcline ($KAlSi_3O_8$). In contrast, the marble waste exhibits stronger peaks of calcite ($CaCO_3$) and dolomite ($CaMg(CO_3)_2$), accompanied by less intense peaks of quartz and muscovite.

Figure 2.1- XRD analysis: (a) granite waste pigment; (b) marble waste pigment.



(a) (b)

The environmentally friendly solvent used in this study was water, with a specific density of 1.00 g/cm³ and a pH ranging between 6.0 and 7.0. The binder selected for this work was the polyvinyl acetate (PVA) resin Cascola Cascorez Extra, characterized by a density of 1.05 g/cm³, a pH within the range of 4.0-5.0, a solids content of 45%, and a viscosity ranging from 6000 to 8000 mPa·s.

The selected biocide was Preservante BAC, formulated with Isothiazolinones and Semi Acetal, offering broad-spectrum protection against bacteria, filamentous fungi, and yeast. This additive comprises a blend of 5-chloro-2-methyl-4-isothiazolin-3-one (CIT), 2-methyl-4-isothiazolin-3-one (MIT), and Semi Acetal. Its primary characteristics include a density of 1.03 g/cm³ and a pH of 3.5, with full solubility in water. Typical dosages range from 0.05 to 0.40% of the total product mass, depending on the desired level of preservation and environmental conditions (WANA QUIMICA, 2023).

The selected dispersant, WANPEX 1450, serves as a controlled molecular weight polymeric dispersant designed for inorganic solid substances such as calcium carbonate, kaolin, clays, talc, titanium dioxide, and others. This additive is composed of Sodium Salt of Polyacrylic Acid. Its primary characteristics include a density of 1.20 g/cm³, a solids content of 35.4%, and a pH of 7.5, with complete solubility in water. Standard concentrations typically range from 0.02 to 1.50% of the total product mass, depending on the specific application requirements (WANA QUIMICA, 2023).

2.2. Experimental model

A quaternary mixture design was used in this study, enabling the investigation of the impacts of mixture components on different response variables and the derivation of equations that elucidate mixture behavior (MENEZES *et al.*, 2010).

The four mixture components subjected to variations in this statistical design were the granite and marble waste contents ranging from 0 to 100%; biocide content ranging from 0 to 1.00%; and dispersant content ranging from 0 to 4.00%. The ranges of additive contents were determined based on maximum specifications set by manufacturers for concentrations based on the total paint mass, as outlined in section 2.1. These specifications were recalculated considering the mass of pigments. Table 2.3 presents the mix proportions of the 27 samples generated using a statistical design of extreme vertices with a degree of 3, including the addition of a central point.

Table 2.3- Proportions of paint components generated in the statistical software Minitab® 17.

SAMPLE	GW	MW	BIOC.	DISP.
GW	1.000			
GW+B_{MED}	0.995		0.005	
GW+B_{MAX}	0.990		0.010	
GW+D_{MED}	0.980			0.020
GW+D_{MAX}	0.960			0.040
GW+B_{MED}+D_{MED}	0.975		0.005	0.020
GW+B_{MAX}+D_{MED}	0.970		0.010	0.020
GW+B_{MED}+D_{MAX}	0.955		0.005	0.040
GW+B_{MAX}+D_{MAX}	0.950		0.010	0.040
MW		1.000		
MW+B_{MED}		0.995	0.005	
MW+B_{MAX}		0.990	0.010	
MW+D_{MED}		0.980		0.020
MW+D_{MAX}		0.960		0.040
MW+B_{MED}+D_{MED}		0.975	0.005	0.020
MW+B_{MAX}+D_{MED}		0.970	0.010	0.020
MW+B_{MED}+D_{MAX}		0.955	0.005	0.040
MW+B_{MAX}+D_{MAX}		0.950	0.010	0.040
GW+MW	0.500	0.500		
GW+MW+B_{MED}	0.498	0.498	0.005	
GW+MW+B_{MAX}	0.495	0.495	0.010	
GW+MW+D_{MED}	0.490	0.490		0.020
GW+MW+D_{MAX}	0.480	0.480		0.040
GW+MW+B_{MED}+D_{MED}	0.488	0.488	0.005	0.020
GW+MW+B_{MAX}+D_{MED}	0.485	0.485	0.010	0.020
GW+MW+B_{MED}+D_{MAX}	0.478	0.478	0.005	0.040
GW+MW+B_{MAX}+D_{MAX}	0.475	0.475	0.010	0.040

Notes- GW: granite waste; MW: marble waste; BIOC.: biocide additive; DISP.: dispersant additive; B_{MED}: biocide additive added in average percentage to the mixture; B_{MAX}: biocide additive added in maximum percentage to the mixture; D_{MED}: dispersant additive added in average percentage to the mixture; D_{MAX}: dispersant additive added in maximum percentage to the mixture.

The amount of resin added to each mixture was set at 50% of the pigment mass, based on the optimization study developed by Lopes *et al.* (2024). The water content was adjusted to maintain viscosity within a constant range suitable for paint application. Through preliminary testing, it was established that the ideal kinematic viscosity of the paints corresponded to a flow time of 23±1 seconds, as measured by a Ford cup viscometer with orifice number 4, following the test methodology outlined in NBR 5849 (ABNT, 2015).

2.3. Preparation of paint samples

To produce the paints, pigments derived from granite and/or marble residues were dispersed in water and subsequently blended with biocide and/or dispersant additives. The contents of pigments and additives were adjusted according to the proportions specified in Table 2.3. The mixture was prepared using a mechanical stirrer and a Cowles disk, operating for 10 minutes at 600 rpm. Then, PVA resin was added and mixed for an additional 10 minutes at 300 rpm.

The viscosity of the paint was measured using a Ford cup viscometer with orifice number 4. Whenever required, viscosity adjustments were made by adding one or more components to the mixture. After that, the mixture was stirred, and viscosity was re-evaluated until a flow time of 23±1 seconds was achieved. All adjustments maintained the predefined proportions of waste and additives specified in Table 2.3. Table 2.4 displays the final compositions of each paint sample, along with the average flow time of the mixture measured using the Ford cup viscometer.

Table 2.4- Mass of paint components and kinematic viscosity of the mixtures.

SAMPLE	GW (g)	MW (g)	WATER (g)	RESIN (g)	BIOC. (g)	DISP. (g)	KV (s)
GW	500.00		377.42	250.00			23.93
GW+B_{MED}	500.00		376.20	250.00	2.51		23.43
GW+B_{MAX}	500.00		370.13	250.00	5.05		23.54
GW+D_{MED}	500.00		362.81	250.00		10.20	22.82
GW+D_{MAX}	500.00		358.63	250.00		20.83	23.68
GW+B_{MED}+D_{MED}	500.00		355.63	250.00	2.56	10.26	23.27
GW+B_{MAX}+D_{MED}	500.00		354.43	250.00	5.15	10.31	23.82
GW+B_{MED}+D_{MAX}	500.00		351.37	250.00	2.62	20.94	23.91
GW+B_{MAX}+D_{MAX}	500.00		355.22	250.00	5.26	21.05	22.12
MW		500.00	335.13	250.00			22.83
MW+B_{MED}		500.00	364.80	250.00	2.51		22.24
MW+B_{MAX}		500.00	330.50	250.00	5.05		22.89
MW+D_{MED}		500.00	268.09	250.00		10.20	23.76
MW+D_{MAX}		500.00	255.31	250.00		20.83	23.89
MW+B_{MED}+D_{MED}		500.00	260.69	250.00	2.56	10.26	23.81
MW+B_{MAX}+D_{MED}		500.00	259.37	250.00	5.15	10.31	23.99
MW+B_{MED}+D_{MAX}		500.00	249.30	250.00	2.62	20.94	23.79
MW+B_{MAX}+D_{MAX}		500.00	247.40	250.00	5.26	21.05	23.92
GW+MW	250.00	250.00	367.44	250.00			23.05
GW+MW+B_{MED}	250.00	250.00	337.90	250.00	2.51		23.35

GW+MW+B_{MAX}	250.00	250.00	315.02	250.00	5.05		23.55
GW+MW+D_{MED}	250.00	250.00	269.78	250.00		10.20	23.99
GW+MW+D_{MAX}	250.00	250.00	253.57	250.00		20.83	23.85
GW+MW+B_{MED}+D_{MED}	250.00	250.00	289.00	250.00	2.56	10.26	23.81
GW+MW+B_{MAX}+D_{MED}	250.00	250.00	268.85	250.00	5.15	10.31	23.87
GW+MW+B_{MED}+D_{MAX}	250.00	250.00	288.65	250.00	2.62	20.94	23.79
GW+MW+B_{MAX}+D_{MAX}	250.00	250.00	284.91	250.00	5.26	21.05	23.41

Notes: GW: granite waste; MW: marble waste; BIOC.: biocide additive; DISP.: dispersant additive; B_{MED}: biocide additive average mixture percentage; B_{MAX}: biocide additive maximum mixture percentage; D_{MED}: dispersant additive average mixture percentage; D_{MAX}: dispersant additive maximum mixture percentage; KV: kinematic viscosity measured by determining fluid the flow time through the Ford Cup viscometer with orifice number 4.

2.4. Determination of the characteristics and performance of the paints

A comprehensive characterization of the paint samples was carried out, based on the determination of their solids content (ASTM-D 3723-05, 2017) and pH, using a TECNOPON brand pH meter (model mPA-210).

To evaluate the effects of the dispersant content, the degree of pigment dispersion in the paint was assessed using a grindometer (model 155-01), following the guidelines of D1210-05, (ASTM, 2022). Plastic viscosity was determined using a rotational Couette viscometer, in accordance with ISO 10414-1 (ISO, 2008). Additionally, selected samples were subjected to zeta potential analysis, using the Malvern Zeta Sizer NanoSeries equipment. This analysis was conducted on solutions of water, waste, and additives in the same proportions used to produce the paints, diluted in deionized water at a ratio of 1:100 (by mass). The pH of the solution was adjusted using HCl to maintain the pH range of the paints.

To evaluate the impact of the biocide, the resistance to bacterial growth was assessed by counting bacterial colony forming units (CFU) per mL in petri dishes, using the surface method. Paint samples were subjected to the PCA (Plate Count Agar) culture medium and then incubated for 7 days at a temperature of 35 ± 2 ºC. These assessments were conducted following this incubation period, based on the protocol outlined in NBR 15821 (ABNT, 2022c). Furthermore, the color of paint samples stored in containers for twelve months was examined to monitor the microorganism effects. Images (Figure 2.2) were captured throughout this period to evaluate color changes.

Figure 2.2- Images captured from some paint samples after different storage times.

To assess the performance of the paints, two key parameters were determined: hiding power and abrasion resistance. The hiding power of the dry paint was evaluated according to NBR 14942 (ABNT, 2022b), calculated as the maximum covered area (m^2) per unit volume of paint (l), ensuring a contrast ratio of 98.5%. This ratio was achieved by comparing reflectance values measured on the black and white parts of a test card, following the methods outlined by Cardoso et al. (2016). Additionally, resistance to wet abrasion without abrasive paste was assessed following the methodology prescribed by NBR 15078 (ABNT, 2006), based on the determination of the number of cycles a paint film can withstand until at least 80% of the area covered by the brush is worn away.

Lastly, scanning electron microscope (SEM) images were captured from selected samples, using the Leo 1430VP equipment. In addition, the roughness of the paint film was measured with a 3D optical profilometer (model Contour GTK).

2.5. Statistical analysis

The results of the paint performance tests were used to elaborate polynomial models that describe each response variable as a function of the independent variables of the mixture design. Subsequently, the proportions of each component were defined to guarantee appropriate values of hiding power (minimum of 4 m^2/l) and abrasion resistance (minimum of 100 cycles) for paints required by NBR 15079-1 (ABNT, 2021).

Additionally, an analysis of variance (ANOVA) was conducted to assess if there was a significant difference in the treatments with biocide and dispersant. To validate the ANOVA results, the homogeneity of variances between treatments and the normality of residuals were checked. The Tukey test was used to compare and identify the means that showed significant differences between the treatments, considering a confidence interval of 95%. Thus, it was possible to determine the percentage of biocide necessary to ensure resistance to fungi and bacteria, as well as the percentage of dispersant required to improve the dispersion of pigment particles.

3. RESULTS AND DISCUSSION

Table 2.5 presents the characterization and performance results of the paints. Furthermore, Table 2.6 showcases the polynomial models obtained for the different response variables, in terms of the independent variables considered in the present experimental design, along with their determination coefficients (R^2).

Table 2.5- Characteristics and properties of paints.

PAINT SAMPLE	SC (%)	pH	PV (cP)	DD (Hg)	BG (CFU/ml)	AR (cycles)	HP (m²/l)
GW	54.77	7.29	84.00	7.30	$4.6.10^{6}$	129	5.50
GW+B_{MED}	53.22	6.99	79.00	7.30	$1.0.10^{2}$	132	5.41
GW+B_{MAX}	54.65	6.99	79.00	7.30	$<1.0.10^{1}$	135	5.16
GW+D_{MED}	58.88	7.84	75.00	7.50	$3.6.10^{7}$	65	5.91
GW+D_{MAX}	58.39	8.18	80.00	7.90	$6.4.10^{7}$	60	6.12
GW+B_{MED}+D_{MED}	58.22	7.65	78.00	7.60	$6.5.10^{1}$	75	5.68
GW+B_{MAX}+D_{MED}	58.24	7.51	83.00	7.70	$<1.0.10^{1}$	102	5.51
GW+B_{MED}+D_{MAX}	59.67	8.06	83.00	7.80	$1.4.10^{2}$	65	5.95
GW+B_{MAX}+D_{MAX}	59.62	8.21	69.00	7.80	$<1.0.10^{1}$	62	5.52
MW	56.58	7.54	47.00	7.50	$2.8.10^{6}$	106	4.01
MW+B_{MED}	54.98	7.26	44.00	7.60	$4.5.10^{2}$	112	3.93
MW+B_{MAX}	56.45	7.17	48.00	7.70	$1.5.10^{2}$	116	3.63
MW+D_{MED}	60.83	7.97	66.00	7.90	$>3.0.10^{7}$	47	4.32
MW+D_{MAX}	60.32	8.17	79.00	8.10	$>3.0.10^{7}$	35	4.46
MW+B_{MED}+D_{MED}	60.14	7.78	75.00	7.90	$2.5.10^{3}$	55	4.08
MW+B_{MAX}+D_{MED}	60.16	7.67	81.00	7.80	$6.5.10^{2}$	3	3.92
MW+B_{MED}+D_{MAX}	61.64	8.21	73.00	8.20	$3.1.10^{3}$	29	4.34
MW+B_{MAX}+D_{MAX}	61.59	8.03	79.00	8.20	$7.1.10^{2}$	25	4.02
GW+MW	54.85	7.44	60.00	7.40	$3.5.10^{6}$	132	4.32
GW+MW+B_{MED}	56.11	7.25	67.00	7.50	$3.1.10^{2}$	135	4.35
GW+MW+B_{MAX}	57.22	7.62	72.00	7.60	$1.8.10^{2}$	138	4.12
GW+MW+D_{MED}	59.92	7.96	89.00	8.10	$>3.0.10^{7}$	90	4.52
GW+MW+D_{MAX}	61.14	8.37	78.00	8.50	$>3.0.10^{7}$	35	4.81
GW+MW+B_{MED}+D_{MED}	58.75	7.83	75.00	8.00	$>3.0.10^{4}$	95	4.61
GW+MW+B_{MAX}+D_{MED}	59.54	7.83	79.00	8.00	$3.9.10^{2}$	75	4.32
GW+MW+B_{MED}+D_{MAX}	58.31	8.18	77.00	8.10	$>3.0.10^{4}$	35	4.67
GW+MW+B_{MAX}+D_{MAX}	58.56	8.12	73.00	8.10	$5.6.10^{2}$	27	4.65

Notes - SC: solids content; PV: plastic viscosity; DD: degree of dispersion; BG: bacterial growth; AR: abrasion resistance; HP: hiding power.

Table 2.6- Valid polynomial models for the series of paints with granite and marble waste pigments.

Regression equations	R^2
SC = 54a + 56b + 140c – 3713d + 4060ad + 4066bd	87.47%
pH = 7.28a + 7.40b – 10.36c + 29.53d + 0.64ab	92.38%
PV = 78a + 47b + 486c – 17197d + 17964ad + 18826bd	80.38%
DD = 7.27a + 7.57b + 7.55c + 22.83d + 0.81ab	88.76%
BG = $1.57.10^7$a + $4.10.10^6$b + $5.07.10^{11}$c + $7.95.10^8$d - $5.13.10^{11}$ac – $5.12.10^7$bc – $6.07.10^{11}$cd	84.46%
AR= 136a + 106b + 299c -1996d	88.24%
HP= 5.61a + 4.09b – 30.08c + 15.99d -1.57ab	98.65%

Notes: a- granite waste; b- marble waste; c- biocidal additive; d- dispersant additive.

The results show that the selected additives changed the characteristics and properties of paints containing granite and marble waste. According to Table 2.6, the interaction between the additives was not significant for most of the properties analyzed. Table 2.7 presents comparisons between treatments obtained from ANOVA and Tukey test.

Table 2.7- Results of paired Tukey comparisons (95% confidence from ANOVA).

Additive		SC	pH	PV	DD	BG	AR	HP
Bioc.	0.000	A	A	A	A	A	A	A
	0.005	A	B	A	A	B	A	A
	0.010	A	B	A	A	B	A	A
	0.000	B	A	A	A	A	A	A
Disp.	0.020	B	B	B	B	B	B	A
	0.040	A	C	B	C	B	C	A

3.1. Solids content (SC)

The solids content (SC) was mainly influenced by the dispersant additive and the type of pigment. Marble waste typically has larger particle dimensions and a smaller specific surface area compared to granite waste. As a result, less water was needed to attain the desired kinematic viscosity, leading to a higher solids content. According to Olhero and Ferreira (2004), the viscosity of suspensions increases with the addition of fine particles, imposing some practical limitations in terms of volume fraction of fines that can be added to the mixture.

Moreover, the dispersant additive played a role in diminishing the water content in the mixture, thereby boosting SC. This effect could be attributed to the adsorption of dispersant additives at the interface of pigment particles, forming a membrane around these particles (LOKHANDE; JAGTAP, 2016b). According to Table 2.7, the biocide did not affect the SC significantly. However, the dispersant caused significant changes in this property at its maximum or intermediate concentrations.

The SC of the paints ranged from 53.22 to 61.54%. Typically, commercially available latex PVA paints have solids content ranging from 35.6 to 52% (SILVA; UEMOTO, 2005). Thus, the paints produced in this study demonstrated a significantly higher solids content, contributing to sustainable development. This is attributed to reduced water contents and increased utilization of waste materials in the production of the paints.

3.2. pH

Based on Table 2.6, the pH of the paints was positively influenced by the dispersant additive (pH=7.5) and negatively influenced by the biocide additive (pH=3.5). Table 2.7 shows that the biocide and the dispersant caused significant changes in pH. Dissolving the biocide additive in water promoted the release of H^+ ions, tending to neutralize the alkaline pH of the paints. Conversely, the dispersant additive released more OH^- ions into the solution, making the paint more alkaline. Values of pH can affect viscosity, pigment stability, paint stability, hydrolytic stability of resins, and the growth of fungi and bacteria (ETIM; ANTAI, 2014).

All paints showed a pH ranging from 7 to 8.5 due to the alkaline pH of granite (pH= 8.9) and marble (pH=9.5) waste. According to Karlsson et al. (2019), water-based decorative paints typically have a pH in the range of 7-9. However, under acidic conditions, they inhibit bacterial growth and enhance the hydrolytic stability of the PVA resin (SAMYN; BOSMANS; COSEMANS, 2021; SUMA; JACOB; JOSEPH, 2009).

3.3. Plastic viscosity (PV)

Values of plastic viscosity (PV) ranged from 44 to 89 cP, despite the fixed kinematic viscosity (KV). This indicates that, within this study, no correlation existed between these two parameters. Paints containing marble waste displayed lower viscosity, even when presenting higher solids content. This underscores the significant influence of the physical characteristics of the pigment on plastic viscosity. Smaller specific surface areas resulted in decreased particle collisions and, consequently, lowered viscosity.

According to Table 2.7, the biocide additive did not cause any significant change in PV. Moreover, the use of average or maximum contents of dispersant additive caused the same effects on this property. The incorporation of the dispersant additive into the mixture generally increased the PV. As expected, higher solids content led to elevated viscosity values (BORLAF *et al.*, 2020). It is noteworthy that the regression equation for PV describes a parabolic behavior, indicating a significant interaction between the dispersant and the pigment particles. This suggests that during the dispersion process, exceeding a certain amount of dispersing agent leads to a decrease in interactions between pigment particles and, consequently, a plastic viscosity reduction (LOKHANDE; JAGTAP, 2016a).

3.4. Degree of dispersion (DD) and zeta potential

The degree of dispersion (DD) was predominantly influenced by the dispersant additive, which fulfilled its function of maintaining the space between pigment particles through electrostatic repulsion or steric hindrance. A DD equal to or greater than 7 Hg represents a good dispersion quality of the pigment in the paste (KAMMER, 2017). Therefore, it is evident that all paints already exhibited satisfactory pigment dispersion. This is largely attributed to the stable characteristics of rock fragments, which do not tend to readily form agglomerates. However, the use of the dispersant additive led to improvements in the dispersion degree of the mixture by around 10%.

Table 2.8 shows the zeta potential results of solutions containing minimum and maximum contents of waste and additives. Each solution underwent three measurements of zeta potential, resulting in closely aligned values and demonstrating the high quality of the results (low standard deviation values).

Table 2.8- Results of zeta potential for the solutions.

Solution	Average zeta potencial (mV)	Standard deviation (mV)	Tukey test
GW	-58.8	0.8	A
GW+B_{MAX}	-52.2	0.8	A
GW+D_{MAX}	-72.7	0.5	B
MW	-22.8	0.3	C
MW+B_{MAX}	-24.5	0.3	C
MW+D_{MAX}	-4.7	0.5	D
GW+MW	-17.3	0.5	E
GW+MW+B_{MAX}	-20.0	0.7	E

GW+MW+D_{MAX}	-23.4	0.3	E

Notes- GW: granite waste; MW: marble waste; B_{MAX}: biocide additive added in maximum percentage to the mixture; D_{MAX}: dispersant additive added in maximum percentage to the mixture.

The results demonstrate that solutions of GW, MW, and GW+MW displayed particles with negative surface charges. The PVA polymer exhibited a weak negative surface charge across almost the entire pH range due to the presence of isolated carboxylate groups (FUJIMOTO *et al.*, 2021; SANTOS; ALVES; PINTO, 2016). Therefore, combining PVA with water and waste suspensions would cause minimal impact on the zeta potential or even render it more negative, indicating repulsion between PVA and waste particles.

The addition of the biocide additive to the solution caused a minimal change in the zeta potential, indicating its concentration may be insufficient to produce significant effects, as confirmed by the Tukey test results. When the dispersant additive was introduced, GW and MW exhibited antagonistic behavior. The dispersant increased the negative charge in the GW solution, decreased it in the MW solution, and induced an intermediate behavior in the GW+MW solution, resulting in a slight increase in the negative charge. This underscores the significant influence of solution conductivity, ion concentration, material composition, pH, and temperature on the zeta potential (KEPEKÇI; YENER İLÇE; DEMIR KANMAZALP, 2021).

The zeta potential serves as a crucial parameter for studying the stability of colloidal suspensions, particularly in terms of evaluation of electrostatic stabilization mechanisms (KEPEKÇI; YENER İLÇE; DEMIR KANMAZALP, 2021; SALEH, 2022). An absolute zeta potential value greater than 30 mV indicates good stability, while a value below 30 mV suggests tendencies toward aggregation, instability, flocculation, or coagulation (PATE; SAFIER, 2016). This underscores the significant role of the dispersant in enhancing the stability of colloidal suspensions, even when individual components exhibit conflicting tendencies. Based on Table 2.8, only the mixtures with granite waste alone (GW, GW+Dmax, and GW+Bmax) showed good stability based on the zeta potential.

3.5. Bacteria growth (BG) and color assessments

Water-based paints are susceptible to biological contamination by microorganisms, which require specific conditions for their development and reproduction, including pH, exposure to sunlight, oxygen availability, nutrients, temperature, and water (ADETUNJI, 2023). According to Fazenda (2009), bacteria can thrive in a pH range varying from 2.0 to 13.0, while fungal growth is more favorable in acidic environments. Hence, this study exclusively focused on bacterial colony counts.

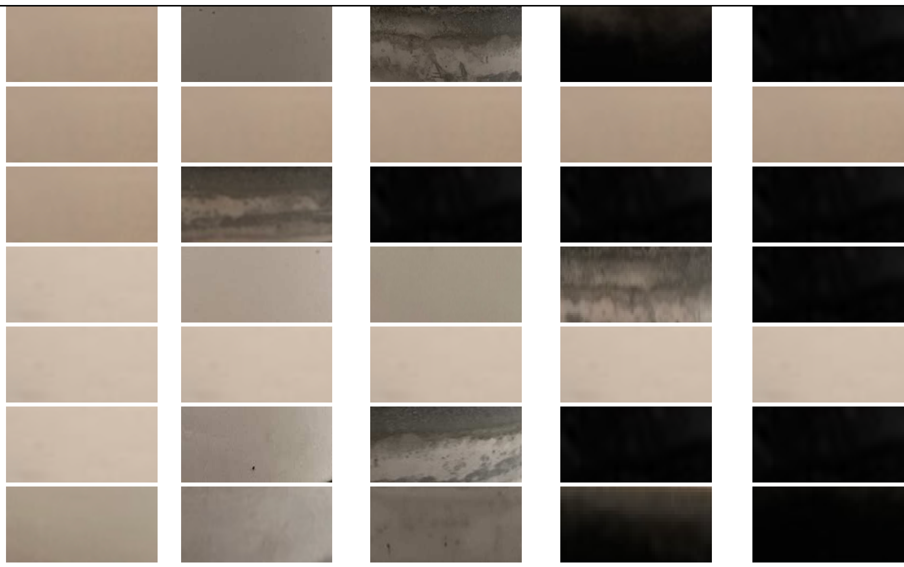
All paint samples without the biocide additive exhibited significant levels of bacterial contamination, with counts reaching values around 10^6, particularly of Pseudomonas. This quantity is sufficient to cause changes in the paints. Furthermore, the use of the dispersant additive resulted in an increase of more than tenfold in bacterial growth (BG). This may be associated with the rise in the pH of the paints in the presence of this additive.

The biocide additive was effective across all formulations, resulting in a significant reduction in the proliferation of microorganisms, particularly in GW paints. Average biocide additive contents reduced bacterial proliferation by over 10^4 times in paints without dispersant. In mixtures containing dispersant additive, the maximum content of biocide was necessary to control the BG indicator.

Table 2.9 displays the results of color assessment for paints packaged at various ages. Only the paints containing biocide showed no noticeable color changes over a storage period of one year. This underscores the importance of incorporating effective biocides in paint formulations to prolong shelf-life and prevent microorganism contamination. The benefits provided by the biocide inclusion were evident, as paints without biocides exhibited noticeable color changes after a storage period of 30 days and complete contamination after 90 days.

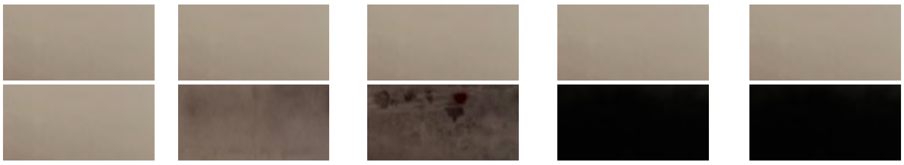
Table 2.9- Colors of the paints determined by the RGB standard after different storage times.

Paint Sample	Color				
	1 day	30 days	90 days	180 days	360 days
GW					
GW+B$_{MAX}$					
GW+D$_{MAX}$					
MW					
MW+B$_{MAX}$					
MW+D$_{MAX}$					
GW+MW					



GW+MW+B_{MAX}

GW+MW+D_{MAX}

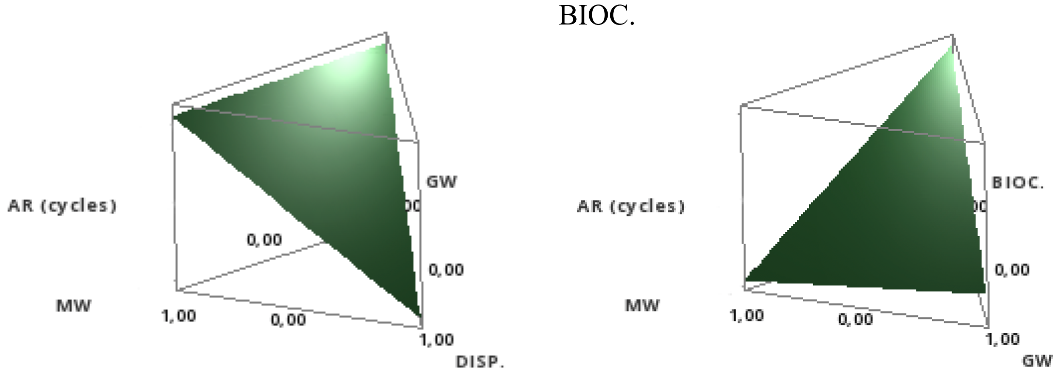


Notes- GW: granite waste; MW: marble waste; B_{MAX}: biocide additive added in maximum percentage to the mixture; D_{MAX}: dispersant additive added in maximum percentage to the mixture.

3.6. Abrasion resistance (AR)

Figures 2.3 and 2.4 show the influence of the biocidal and dispersant additive on the abrasion resistance of the paints. The presence of the dispersant additive significantly compromised abrasion resistance (AR), according to Figure 2.3a) and Tables 2.6 and 2.7. This can be attributed to the dispersant additives' ability to bind to the pigment surface through their anchoring functional groups, leading to increased electrostatic repulsion between particles (FARROKHPAY et al., 2010). Paints with high levels of dispersant additive experienced a reduction of more than 70% in their AR indicator, making their use impractical, especially in high concentrations.

Figure 2.3- Surface graph of AR for component trios: a) GW, MW, and DISP.; b) GW, MW, and BIOC.

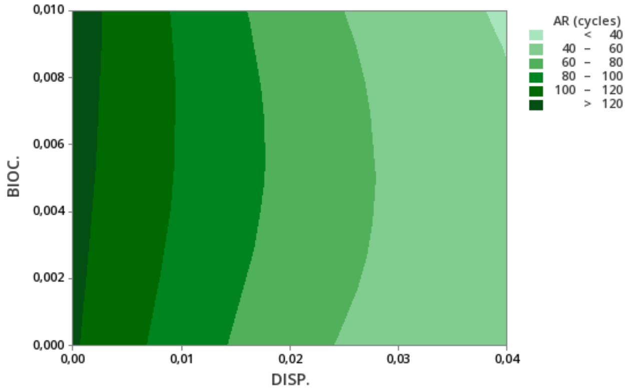


(a) (b)

Furthermore, Figure 2.3b shows that the biocide additive tends to increase the abrasion resistance of the paints, possibly due to its more acidic pH, as lower pH levels enhance the hydrolytic stability of the resin (YAMAK, 2013; SUMA; JACOB; JOSEPH, 2009). However, since the biocide was used in small concentrations (Table 2.7), AR did not exhibit significant variations with the addition of the biocide additive. This implies that the additive did not enhance the effectiveness of the PVA resin, which is primarily responsible for the paint's wear resistance.

According to NBR 15079-1 (ABNT, 2021), economical paints must demonstrate a minimum of 100 cycles of resistance to wet abrasion without abrasive paste. The results indicated that all samples without the dispersing additive met this requirement. This raises concerns regarding the inclusion of this additive in paint compositions (Figure 2.4).

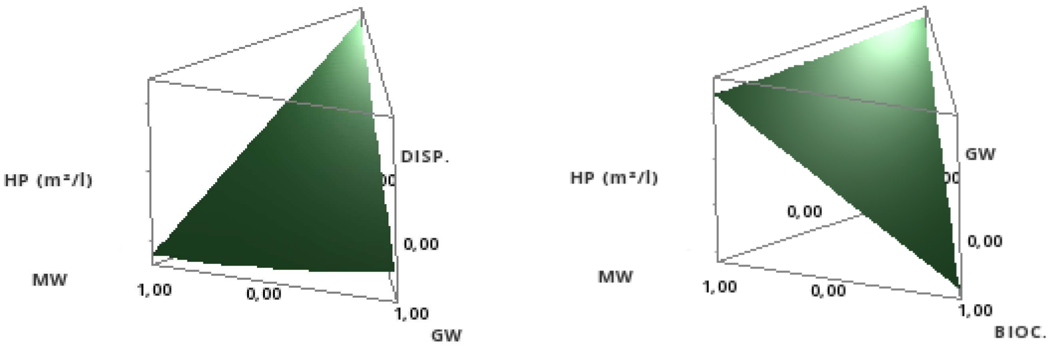
Figure 2.4- Contour plot of AR versus BIOC and DISP.



3.7. Hiding power (HP)

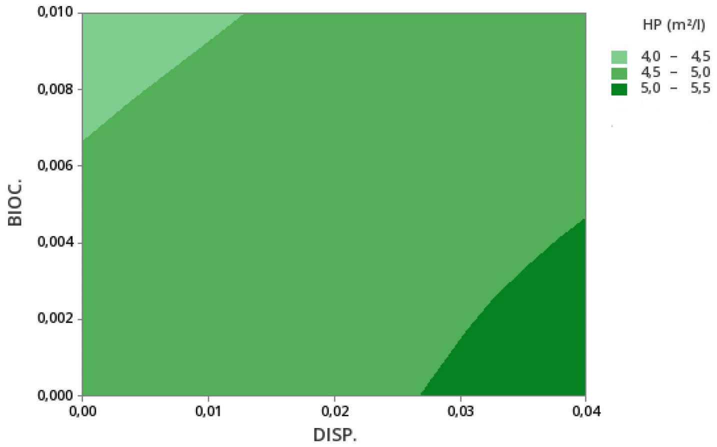
Figures 2.5 and 2.6 show the influence of the biocidal and dispersant additive on the hiding power (HP) of the paints. In contrast to the abrasion resistance (AR) results, the HP was positively impacted by the presence of the dispersant additive, according to Figure 2.5a and Table 2.6. This is attributed to improved dispersion, which enhances the paint's ability to conceal the substrate surface, as indicated by Brząkalski et al. (2022)

Figure 2.5- Surface graph of HP for component trios: a) GW, MW, and DISP.; b) GW, MW, and BIOC.



(a) (b)

Figure 2.6- Contour plot of HP versus BIOC and DISP.



On the other hand, Figure 2.5b and Table 2.6 show that the biocide additive had a negative impact on HP. However, even for the maximum biocide content, the opacity losses in the paint films were less than 10%. It is essential to emphasize that the biocide additive was introduced into the mixtures to preserve the shelf life of canned paint and the integrity of the dry film.

Overall, Table 2.7 revealed that the presence of the biocide and dispersant additives did not significantly affect the optical performance of the paints.

According to NBR 15079-1 (ABNT, 2021), economical paints must demonstrate a minimum of 4 m^2/l of hiding power of dry paint. It is clear that virtually all paint samples met this quality requirement (Figure 2.6). Higher values of solids content lead to thicker paint films, thereby providing better coverage.

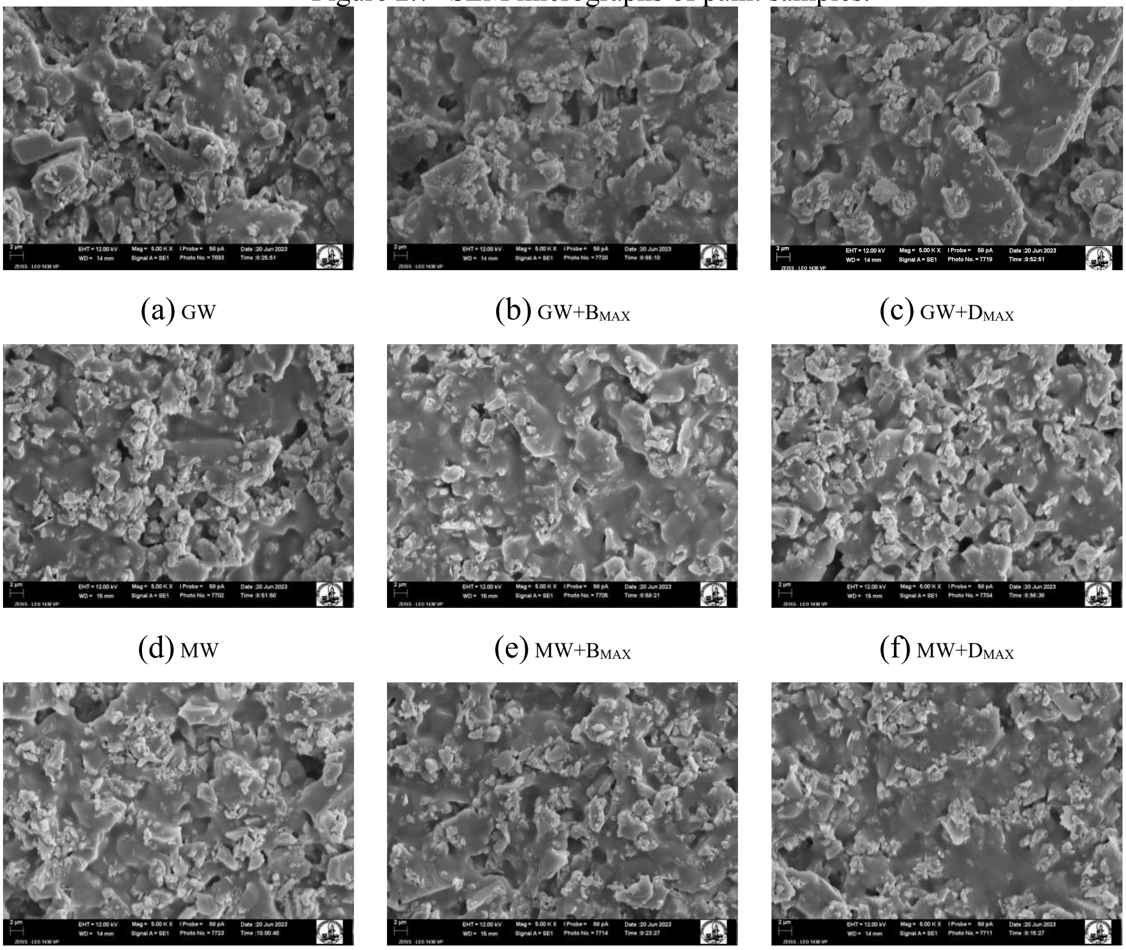
3.8. Microscopic analyses

Figure 2.7 presents the SEM images and Table 2.10 provides the roughness of paint films with minimum and maximum contents of waste and additives.

The SEM images and roughness results did not reveal significant differences among the samples without additives, samples with biocide additives, and samples with dispersant additives. This is primarily due to the low concentration of additives added to the paints, which is less than 1% of their total mass. Paints with the maximum amount of dispersant showed a slight reduction in roughness, which can be attributed to the dispersant's characteristic of preventing particle agglomeration, resulting in a more uniform paint film with greater coverage.

This improvement in uniformity was evident in the SEM micrographs by the reduction of voids compared to the other samples.

Figure 2.7- SEM micrographs of paint samples.



(a) GW (b) GW+B_{MAX} (c) GW+D_{MAX}

(d) MW (e) MW+B_{MAX} (f) MW+D_{MAX}

(g) GW+MW (h) GW+MW+B_{MAX} (i) GW+MW+D_{MAX}

Table 2.10- Roughness of paint samples.

Paint sample	Roughness (μm)		
	First determination	Second determination	Third determination
GW	3.46	3.54	3.48
GW+B_{MAX}	3.51	3.55	3.52
GW+D_{MAX}	3.41	3.44	3.39
MW	4.57	4.49	4.51
MW+B_{MAX}	4.60	4.52	4.55
MW+D_{MAX}	4.55	4.52	4.47
GW+MW	3.75	3.81	3.72
GW+MW+B_{MAX}	3.79	3.84	3.75
GW+MW+D_{MAX}	3.68	3.72	3.70

4. CONCLUSION

In summary, the study highlighted the considerable influence of additives on diverse properties of water-based paints containing marble and granite waste. The main findings are as follows:

- The solids content increased due to the dispersant and the type of pigment, promoting sustainability by reducing the required water content and enhancing the recycling of waste materials.

- The pH of the paint was influenced by the incorporation of the dispersant additive, leading to higher pH values. In contrast, the inclusion of the biocide additive contributed to paints with a lower pH.

- Plastic viscosity exhibited variations, revealing the interplay between the dispersant, pigment particles, and solids content.

- The degree of pigment dispersion was positively affected by the dispersant, resulting in an improvement in the mixture.

- The biocide additive effectively controlled bacterial growth, emphasizing its pivotal role in preserving paint quality.

- Dispersant additives affected the abrasion resistance of paints. Therefore, this study emphasized the importance of careful use of high concentrations of dispersant additives, as they significantly reduced the abrasion resistance of the paints.

- The biocide did not significantly impact either the hiding power or the abrasion resistance of the paints.

In conclusion, this study provides valuable insights into the effects of dispersant and biocide additives on different properties of paints produced with granite and marble waste, offering guidance for the formulation of sustainable and performance-satisfactory paints.

REFERENCES

ADETUNJI, A. Bacteria Contamination of Fresh Water-Based Paint Samples. **Preprints** , 2023.

AMERICAN SOCIETY FOR TESTING AND MATERIALS. **ASTM D 3723**-05: Standard Test Method for Pigment Content of Water-Emulsion Paints by Low-Temperature Ashing. West Conshohocken, PA, 2017.

AMERICAN SOCIETY FOR TESTING AND MATERIALS. **ASTM D1210-05.** Standard Test Method for Fineness of Dispersion of Pigment-Vehicle Systems by Hegman-Type Gage. West Conshohocken, PA, 2022.

ASSOCIAÇÃO BRASILEIRA DE NORMAS TÉCNICAS. **NBR 13600:** Solo - Determinação do teor de matéria orgânica por queima a 440 °C. Rio de Janeiro, 2022.

ASSOCIAÇÃO BRASILEIRA DE NORMAS TÉCNICAS. **NBR 16605:** Cimento Portland e outros materiais em pó — Determinação da massa específica. Rio de Janeiro, 2017.

ASSOCIAÇÃO BRASILEIRA DE NORMAS TÉCNICAS. **NBR 5849:** Tintas — Determinação de viscosidade pelo copo Ford. Rio de Janeiro, 2015.

ASSOCIAÇÃO BRASILEIRA DE NORMAS TÉCNICAS. **NBR 14942:** Tintas para construção civil - Método para avaliação de desempenho de tintas para edificações não industriais - Determinação do poder de cobertura de tinta seca e rendimento teórico. Rio de Janeiro, 2019a.

ASSOCIAÇÃO BRASILEIRA DE NORMAS TÉCNICAS. **NBR 15078:** Tintas para construção civil - Método para avaliação de desempenho de tintas para edificações não industriais - Determinação da resistência à abrasão úmida sem pasta abrasiva. Rio de Janeiro, 2006.

ASSOCIAÇÃO BRASILEIRA DE NORMAS TÉCNICAS. **NBR 15079-1:** Tintas para construção civil — Requisitos mínimos de desempenho - Parte 1: Tinta látex fosca nas cores claras. Rio de Janeiro, 2019b.

ASSOCIAÇÃO BRASILEIRA DE NORMAS TÉCNICAS. **NBR15821:** Tintas para construção civil — Método para avaliação de desempenho de tintas para edificações não industriais — Determinação do grau de resistência de tintas, vernizes e complementos, em emulsão na embalagem ao ataque de micro-organismos. Rio de Janeiro, 2022c.

ATIGANYANUN, S.; KUMNORKAEW, P. Effects of pigment volume concentration on radiative cooling properties of acrylic-based paints with calcium carbonate and hollow silicon dioxide microparticles. **International Journal of Sustainable Energy**, vol. 42, no. 1, p. 612–626, 14 Dec. 2023. https://doi.org/10.1080/14786451.2023.2221082.

AZEVEDO, G. H. de. Use of the Reply of Caulim'S Benefiting Industries for the Production of Earth-Based Ecological Ink. **Tecnologia em Metalurgia, Materiais e Mineração**, vol. 15, no. 3, p. 242–247, 2018. .

BORLAF, M.; SZUBRA, N.; SERRA-CAPDEVILA, A.; KUBIAK, W. W.; GRAULE, T. Fabrication of ZrO2 and ATZ materials via UV-LCM-DLP additive manufacturing technology. **Journal of the European Ceramic Society**, vol. 40, no. 4, p. 1574–1581, Apr. 2020. DOI 10.1016/j.jeurceramsoc.2019.11.037.

BRZĄKALSKI, D.; PRZEKOP, R. E.; FRYDRYCH, M.; PAKUŁA, D.; DOBROSIELSKA, M.; SZTORCH, B.; MARCINIEC, B. Where ppm Quantities of Silsesquioxanes Make a Difference—Silanes and Cage Siloxanes as TiO2 Dispersants and Stabilizers for Pigmented Epoxy Resins. **Materials**, vol. 15, no. 2, p. 494, 10 Jan. 2022. DOI 10.3390/ma15020494.

CARDOSO, F. P.; ALVARENGA, R. C. S. S.; CARVALHO, A. F.; MENDES, T. S. G. The influence of the specific surface and soil pigment content on the covering power of paints for construction. 2016. **16º SIACOT** [...]. [*S. l.*: *s. n.*], 2016.

CARDOSO, F. de P.; ALVARENGA, R. de C. S. S.; CARVALHO, A. F. de; FONTES, M. P. F. Production process and evaluation of performance requirements of soil pigments based paint for buildings (in portuguese). **Ambiente Construído**, vol. 16, no. 4, p. 167–183, Dec. 2016. DOI 10.1590/s1678-86212016000400112.

DANISH, A.; MOSABERPANAH, M. A.; SALIM, M. U.; FEDIUK, R.; RASHID, M. F.; WAQAS, R. M. Reusing marble and granite dust as cement replacement in cementitious composites: A review on sustainability benefits and critical challenges. **Journal of Building Engineering**, vol. 44, p. 102600, Dec. 2021. DOI 10.1016/j.jobe.2021.102600.

DANKOVÁ, M.; KALENDOVÁ, A.; MACHOTOVÁ, J. Waterborne coatings based on acrylic latex containing nanostructured ZnO as an active additive. **Journal of Coatings Technology and Research**, vol. 17, no. 2, p. 517–529, 3 Mar. 2020. DOI 10.1007/s11998-019-00302-6.

EMBRAPA. Soil Analysis Methods Handbook. **Manual of Soil Analysis Methods - Chapter 8 - Particle Density**, vol. 3rd revise, p. 574, 2017. Available at: https://ainfo.cnptia.embrapa.br/digital/bitstream/item/194786/1/Pt-5-Cap-1-Micromorfologia-do-solo.pdf.

ETIM, L. B.; ANTAI, S. P. The effects of temperature and pH bacterial degradation of latex paint in humid environment. **Global Journal of Pure and Applied Sciences**, vol. 20, no. 2, p. 89, 8 Dec. 2014. https://doi.org/10.4314/gjpas.v20i2.2.

FARROKHPAY, Saeed; MORRIS, Gayle E.; FORNASIERO, Daniel; SELF, Peter. Stabilisation of titania pigment particles with anionic polymeric dispersants. **Powder Technology**, vol. 202, no. 1–3, p. 143–150, Aug. 2010. DOI 10.1016/j.powtec.2010.04.031.

FAZENDA, J. M. R. **Paints: Science and Technology (in portuguese)**. [*S. l.*: *s. n.*], 2009.

FEI, W; OPOKU, A; AGYEKUM, K; OPPON, J. A.; AHMED, V.; CHEN, C.; LOK, K. L. The Critical Role of the Construction Industry in Achieving the Sustainable Development Goals (SDGs): Delivering Projects for the Common Good. **Sustainability**, vol. 13, no. 16, p. 9112, 14 Aug. 2021. DOI 10.3390/su13169112.

FUJIMOTO, K.; YAMAWAKI-OGATA, A.; NARITA, Y.; KOTSUCHIBASHI, Y. Fabrication of Cationic Poly(vinyl alcohol) Films Cross-Linked Using Copolymers Containing Quaternary Ammonium Cations, Benzoxaborole, and Carboxy Groups. **ACS Omega**, vol. 6, no. 27, p. 17531–17544, 13 Jul. 2021. https://doi.org/10.1021/acsomega.1c02013.

GALVÃO, J. L. B.; ANDRADE, H. D.; BRIGOLINI, G. J.; PEIXOTO, R. A. F.; MENDES, J. C. Reuse of iron ore tailings from tailings dams as pigment for sustainable paints. **Journal of**

Cleaner Production, vol. 200, p. 412–422, 2018. https://doi.org/10.1016/j.jclepro.2018.07.313.

GOL, F.; CIBUK, S.; KACAR, E.; SARITAS, Z. G.; YILMAZ, A.; ARSLAN, M.; SEN, F. Evaluation of solid wastes in the manufacture of ceramic tableware glazes. **Ceramics International**, vol. 48, no. 11, p. 15622–15628, Jun. 2022. DOI 10.1016/j.ceramint.2022.02.096.

GUPTA, S.; PUTTAIAHGOWDA, Y. M.; NAGARAJA, A.; JALAGERI, M. D. Antimicrobial polymeric paints: An up-to-date review. **Polymers for Advanced Technologies**, vol. 32, no. 12, p. 4642–4662, 30 Dec. 2021. DOI 10.1002/pat.5485.

YAMAK, H. B. Emulsion Polymerization: effects of polymerization variables on the properties of vinyl acetate based emulsion polymers. **Polymer Science**. [*S. l.*: *s. n.*], 2013.

ISO. **ISO 10414-1:** Petroleum and natural gas industries — Field testing of drilling fluids — Part 1: Water-based fluids. , p. 91, 2008. .

JACOB, J.; GRELIER, S.; GRAU, M.; CHOREIN, B. Effect of Dispersing Agents on the Stability of Recycled Paints. **Coatings**, vol. 12, no. 11, p. 1722, 11 Nov. 2022. DOI 10.3390/coatings12111722.

JOSIAH MARUT, J.; ALAEZI, J. O.; OBEKA, I. C. A Review of Alternative Building Materials for Sustainable Construction Towards Sustainable Development. **Journal of Modern Materials**, vol. 7, no. 1, p. 68–78, 29 Dec. 2020. DOI 10.21467/jmm.7.1.68-78.

KAMMER, E. H. **Influência de resinas alquídicas na dispersão de pigmentos**. 2017.

KARAKAŞ, F.; ÇELIK, M. S. Stabilization mechanism of main paint pigments. **Progress in Organic Coatings**, vol. 123, p. 292–298, Oct. 2018. DOI 10.1016/j.porgcoat.2018.07.019.

KARLSSON, M. C. F.; ABBAS, Z.; BORDES, R.; CAO, Y.; LARSSON, A.; TAYLOR, P.; STEENARI, B. Characterisation of silicon, zirconium and aluminium coated titanium dioxide pigments recovered from paint waste. **Dyes and Pigments**, vol. 162, p. 145–152, Mar. 2019. https://doi.org/10.1016/j.dyepig.2018.06.028.

KEPEKÇI, R. A.; YENER İLÇE, B.; DEMIR KANMAZALP, S. Plant-derived biomaterials for wound healing. [*S. l.*: *s. n.*], 2021. p. 227–264. https://doi.org/10.1016/B978-0-12-819489-8.00001-6.

KORE, S. D.; VYAS, A. K.; KABEER K.I., S. A. A brief review on sustainable utilisation of marble waste in concrete. **International Journal of Sustainable Engineering**, vol. 13, no. 4, p. 264–279, 3 Jul. 2020. DOI 10.1080/19397038.2019.1703151.

LI, Z.; LAO, J.; WANG, L.; LIM, N. S.; TAN, K. H.; QIAN, S. A review on substitution of natural sand with granite fines in sustainable concrete. **Construction and Building Materials**, vol. 346, p. 128417, Sep. 2022. DOI 10.1016/j.conbuildmat.2022.128417.

LOKHANDE, G. P.; JAGTAP, R. N. Design and synthesis of polymeric dispersant for water-borne paint by atom transfer radical polymerization. **Designed Monomers and Polymers**, vol. 19, no. 3, p. 256–270, 2 Apr. 2016a. DOI 10.1080/15685551.2015.1136534.

LOKHANDE, G. P.; JAGTAP, R. N. Modified poly(butyl methacrylate- b -glycidyl methacrylate) dispersant for solvent-based paint by Reverse Atom Transfer Radical Polymerization. **Progress in Organic Coatings**, vol. 90, p. 359–368, Jan. 2016b. DOI 10.1016/j.porgcoat.2015.06.025.

LOPES, M. M.; ALVARENGA, R. de C. S. S.; PEDROTI, L. G.; RIBEIRO, J. C. L.; CARVALHO, A. F. de; CARDOSO, F. de P.; MENDES, B. C. Influence of the incorporation of granite waste on the hiding power and abrasion resistance of soil pigment-based paints. **Construction and Building Materials**, vol. 205, p. 463–474, 2019. https://doi.org/10.1016/j.conbuildmat.2019.02.046.

LOPES, M. M. S.; PEDROTI, L. G.; LIMA, G. E. S. de; RIBEIRO, J. C. L.; NALON, G. H.; MENDES, B. C.; OLIVEIRA, A. L. de. Influence of the Incorporation of Granite Waste on the Weathering Resistance of Soil Pigment-Based Paints. **Characterization of Minerals, Metals, and Materials 2021**. Springer. [*S. l.*: *s. n.*], 2021. p. 471–481. DOI 10.1007/978-3-030-65493-1_47.

LOPES, M. M. S.; PEDROTI, L. G.; OLIVEIRA, A. F. de; RIBEIRO, J. C. L.; CARVALHO, J. M F. de; CARVALHO, A. F. de; CARDOSO, F. de P.; NALON, G. H.; LIMA, G. E. S. de. Optimization of performance of sustainable paints using granite waste through the variation of particle size and pH. **Journal of Cleaner Production**, vol. 326, p. 129418, Dec. 2021. DOI 10.1016/j.jclepro.2021.129418.

LOPES, M.M.S., PEDROTI, L.G., CARVALHO, J.M.F. DE, RIBEIRO, J.C.L., NALON, G.H., MOURA, H.R. de C.V. Optimization of performance of building paints using granite and marble waste. **Ambiente Construído**, 2024. https://doi.org/10.1590/s1678-86212024000100758

MARRAS, G.; CARCANGIU, G.; MELONI, P.; CAREDDU, N. Circular economy in marble industry: From stone scraps to sustainable water-based paints. **Construction and Building Materials**, vol. 325, p. 126768, Mar. 2022. DOI 10.1016/j.conbuildmat.2022.126768.

MENEZES, R. R.; MARQUES, L. N.; CAMPOS, L. A.; FERREIRA, H. S.; SANTANA, L. N. L.; NEVES, G. A. Use of statistical design to study the influence of CMC on the rheological properties of bentonite dispersions for water-based drilling fluids. **Applied Clay Science**, vol. 49, no. 1–2, p. 13–20, Jun. 2010. DOI 10.1016/j.clay.2010.03.013.

NASCIMENTO, A. S.; SANTOS, C. P. dos; MELO, F. M. C. de; OLIVEIRA, V. G. A.; BETÂNIO OLIVEIRA, R. M. P.; MACEDO, Z. S.; DE OLIVEIRA, H. A. Production of plaster mortar with incorporation of granite cutting wastes. **Journal of Cleaner Production**, vol. 265, p. 121808, Aug. 2020. DOI 10.1016/j.jclepro.2020.121808. Available at: https://linkinghub.elsevier.com/retrieve/pii/S0959652620318552.

OBIDI, O.; OKEKUNJO, F. Bacterial and fungal biodeterioration of discolored building paints in Lagos, Nigeria. **World Journal of Microbiology and Biotechnology**, vol. 33, no. 11, p. 196, 5 Nov. 2017. DOI 10.1007/s11274-017-2362-y. Available at: http://link.springer.com/10.1007/s11274-017-2362-y.

OLHERO, S. M; FERREIRA, J. M. F. Influence of particle size distribution on rheology and particle packing of silica-based suspensions. **Powder Technology**, vol. 139, no. 1, p. 69–75, Jan. 2004. DOI 10.1016/j.powtec.2003.10.004. Available at: https://linkinghub.elsevier.com/retrieve/pii/S0032591003003279.

PATE, K.; SAFIER, P. Chemical metrology methods for CMP quality. **Advances in Chemical Mechanical Planarization (CMP)**. [*S. l.*]: Elsevier, 2016. p. 299–325. https://doi.org/10.1016/B978-0-08-100165-3.00012-7.

PIEMONTE, V.; FRANCIONI, F.; CAPOCELLI, M.; PRISCIANDARO, M. BIODEGRADATION OF ACRYLIC PAINTS: PROCESS MODELLING OF BIOCIDE EFFECT ON BIOMASS GROWTH AT DIFFERENT TEMPERATURES. **Brazilian Journal of Chemical Engineering**, vol. 34, no. 2, p. 557–566, Apr. 2017. DOI 10.1590/0104-6632.20170342s20150766.

SALEH, T. A. **Properties of nanoadsorbents and adsorption mechanisms**. [*S. l.*: *s. n.*], 2022. p. 233–263. https://doi.org/10.1016/B978-0-12-849876-7.00010-5.

SAMYN, P.; BOSMANS, J.; COSEMANS, P. Current Alternatives for In-Can Preservation of Aqueous Paints: A Review. 30 Oct. 2021. **The 2nd International Online Conference on Polymer Science—Polymers and Nanotechnology for Industry 4.0** [...]. Basel Switzerland: MDPI, 30 Oct. 2021. p. 18. https://doi.org/10.3390/IOCPS2021-11245.

SANTOS, D. P. dos; ALVES, T. L. M.; PINTO, J. C. Adsorption of BSA (Bovine Serum Albuminum) and lysozyme on poly(vinyl acetate) particles. **Polímeros**, vol. 26, no. 4, p. 282–290, 8 Dec. 2016. https://doi.org/10.1590/0104-1428.2103.

SANTOS NASCIMENTO, E. S.; SOUZA, P. C. de; OLIVEIRA, H. A. de; MELO JÚNIOR, C. M.; OLIVEIRA ALMEIDA, V. G. de; MELO, F. M. C. de. Soil-cement brick with granite cutting residue reuse. **Journal of Cleaner Production**, vol. 321, p. 129002, Oct. 2021. DOI 10.1016/j.jclepro.2021.129002. Available at: https://linkinghub.elsevier.com/retrieve/pii/S0959652621031929.

SILVA, J. M. da; UEMOTO, K. L. Caracterização de tintas látex para construção civil: diagnóstico do mercado do estado de São Paulo. 2005. **Escola Politécnica da Universidade de São Paulo**. Available at: http://dx.doi.org/10.1016/j.cirp.2016.06.001%0Ahttp://dx.doi.org/10.1016/j.powtec.2016.12.055%0Ahttps://doi.org/10.1016/j.ijfatigue.2019.02.006%0Ahttps://doi.org/10.1016/j.matlet.2019.04.024%0Ahttps://doi.org/10.1016/j.matlet.2019.127252%0Ahttp://dx.doi.o.

SINGH CHOUHAN, H.; KALLA, P.; NAGAR, R.; KUMAR GAUTAM, P. Influence of dimensional stone waste on mechanical and durability properties of mortar: A review. **Construction and Building Materials**, vol. 227, p. 116662, Dec. 2019. DOI 10.1016/j.conbuildmat.2019.08.043. Available at: https://linkinghub.elsevier.com/retrieve/pii/S0950061819320720.

SRIVASTAVA, A.; SINGH, S.K. Utilization of alternative sand for preparation of sustainable mortar: A review. **Journal of Cleaner Production**, vol. 253, p. 119706, Apr. 2020. DOI 10.1016/j.jclepro.2019.119706. Available at: https://linkinghub.elsevier.com/retrieve/pii/S0959652619345767.

SUMA, K. K.; JACOB, S.; JOSEPH, R. Paint Formulation Using Water Based Binder and Property Studies. **Macromolecular Symposia**, vol. 277, no. 1, p. 144–151, Feb. 2009. DOI 10.1002/masy.200950318. Available at: http://doi.wiley.com/10.1002/masy.200950318.

TRESSMANN, D. M. G. A.; PEDROTI, L. G.; CARVALHO, A. F. de; RIBEIRO, J. C. L.; CARDOSO, F. de P.; LOPES, M. M. S.; OLIVEIRA, A. F. de; FERREIRA, S. O. Research into the use of marble waste as mineral filler in soil pigment-based paints and as an active pigment in waterborne paints. **Construction and Building Materials**, vol. 241, p. 117976, 2020. DOI 10.1016/j.conbuildmat.2019.117976.

TUGRUL TUNC, E. Recycling of marble waste: A review based on strength of concrete containing marble waste. **Journal of Environmental Management**, vol. 231, p. 86–97, Feb. 2019. DOI 10.1016/j.jenvman.2018.10.034.

WANA QUIMICA. https://wanaquimica.com.br/produtos-2/. 2023. **WANA QUIMICA**. Available at: https://wanaquimica.com.br/produtos-2/. Accessed on: 28 Oct. 2023.

ARTICLE 3.

NATURAL AND ACCELERATED WEATHERING EVALUATION OF GRANITE AND MARBLE WASTE PAINTS

ABSTRACT

Recent studies have highlighted the potential for using waste generated from the processing of granite and marble as pigments in sustainable and low-cost paints. To evaluate the durability of these paints, this work presents an assessment of the resistance to weathering (natural and accelerated) of different formulations of PVA (polyvinyl acetate) latex paints produced with pigments of granite and/or marble waste, with and without the addition of biocidal and/or dispersant additives. Natural weathering tests were conducted in the Brazilian city of Viçosa, Minas Gerais, where mortar slabs covered with paint samples were exposed to a natural weathering process for one year. Accelerated weathering tests were also performed using a weathering chamber that simulates UV radiation, high temperatures, and condensation mechanisms. The specimens were evaluated based on calculations of the delta-E parameter to determine color changes, pull-out tests, and visual and microscopic analyses of possible pathologies in the paint film. The results indicated that the paints only underwent significant color changes, possibly due to resin degradation after exposure to UV radiation and/or bacterial growth. Furthermore, the accelerated weathering chamber was able to replicate one year of natural weathering results in just 17 days.

Keywords: Additives. Durability. Granite waste. Marble waste. Paints. Performance.

1. INTRODUCTION

In recent years, several studies have highlighted the potential for reusing waste generated from the processing of granite and marble as pigments in sustainable and low-cost paints (LOPES *et al.*, 2021a; LOPES *et al.*, 2021b; LOPES *et al.*, 2019; TRESSMANN *et al.*, 2020; MOURA *et al.*, 2023). All of these works were motivated by: (1) the large amount of solid waste generated in the processing of ornamental rocks, especially granite and marble (ALMADA *et al.*, 2023; NAYAK; SATAPATHY; MANTRY, 2022; PEREIRA; CAPUZZO; LAMEIRAS, 2022; SINGH; NAGAR; AGRAWAL, 2016); (2) the numerous chemicals used in the manufacture of paints, which are responsible for generating high concentrations of organic compounds, suspended solids, and dangerous pollutants, such as heavy metals (AJIBOYE; OYEWO; ONWUDIWE, 2021; CHUKWUMA *et al.*, 2022; MANDAL *et al.*, 2020); and (3) the high consumption of building paints in Brazil and around the world (ABRAFATI, 2022). These works especially evaluated basic characteristics and performance of paints produced with granite and/or marble waste. However, in-depth studies were not carried out to investigate the durability of paints exposed to weathering.

In the research field of paints based on granite and marble waste, Lopes *et al.* (2019) and Tressmann *et al.* (2020) conducted different experimental tests of soil-based paints containing these wastes as mineral fillers, observing the potential of reuse of these materials in paint production. Lopes *et al.* (2021) succeeded in enhancing the performance of paints based on granite waste by varying the granulometry of the waste and adjusting the pH of the mixtures. Furthermore, Moura *et al.* (2023) introduced the incorporation of additives into the sustainable paints to improve their dispersion and resistance to bacterial growth, which were the main issues identified in previous studies.

According to Fazenda (2009), paints are polymeric materials comprising pigments, resin, solvent, and additives. The combination of these components determines the resistance and optical properties, type of application, and final cost of the product. In addition, paints must be able to protect the substrate against weathering agents, wear, bacteriological attack, among others.

Weathering resistance tests are important in assessing the usability and quality of materials throughout their lifespan. These tests can be conducted outdoors under natural exposure conditions or in accelerated weathering chambers. Although exposure to natural environments is considered the most reliable and effective method for evaluating the durability of a coating, this process is often time-consuming as it requires time for weathering effects to become evident. Additionally, variable conditions at exposure sites make it difficult to achieve reliable repeatability between experiments. On the other hand, weathering chambers offer the advantage of allowing precise control and adjustment of weathering parameters, ensuring more reliable repeatability. Moreover, accelerated aging chambers aim to simulate, in a short period of time, the degree of damage that could occur over months or years under real conditions. However, the results obtained from weathering chambers have limitations, as only some weathering factors can be precisely reproduced. Therefore, to ensure consistency with service performance, accelerated aging tests should be designed to promote the same failure mechanisms experienced in real service conditions (COGULET; BLANCHET; LANDRY, 2019; CRISTOFORETTI *et al.*, 2023; FRIGIONE; RODRÍGUEZ-PRIETO, 2021; GONZÁLEZ-LÓPEZ *et al.*, 2020; SIAKENG *et al.*, 2020).

Several studies available in the literature used weathering techniques in sustainable and commercial paints. For example, Galvão *et al.* (2018) carried out a natural weathering test on sustainable paints and quantified the material deterioration by determining the film color changes at the end of the exposure period. Allen *et al.* (2018) evaluated the durability of paints using accelerated weathering equipment, which allowed the paint films to be subjected to ultraviolet (UV) radiation, temperature variations and wetting/drying cycles that simulated the effects of rain. These authors quantified the durability of the coating by monitoring its weight. Cogulet, Blanchet and Landry (2019) carried out a durability study on two acrylic paints through external exposure in three different locations (Arizona, Florida and the province of Quebec) and exposure to accelerated weathering. In this study, degradation was characterized by colorimetry and FTIR (Fourier Transform Infrared Spectroscopy) analyses. Large differences were observed in the results obtained from four different weathering methods, highlighting the need to test paints in an end-use environment for accurate assessment of its performance. Tressmann *et al.* (2020), Lopes *et al.* (2021) and Moura *et al.* (2023) also carried out a natural weathering resistance test on sustainable PVA latex paints and evaluated their deterioration through color change and visual analysis to identify pathological manifestations in the paint film after exposure.

Given this context, the objective of this study is to evaluate the resistance to weathering (natural and accelerated) of different formulations of PVA (polyvinyl acetate) latex paints produced with pigments from granite and/or marble waste, with and without the addition of biocidal and/or dispersant additives. This research brings new and important insights into: (1) durability of sustainable and low-cost paints produced with granite and marble waste; (2) influence of biocidal and dispersant additives on the weathering resistance of PVA latex paints; (3) comparison of the weathering resistance of granite and marble waste paints with commercial paints; and (4) comparison between the results of natural and accelerated weathering for different paint formulations, establishing correlations between them.

2. MATERIALS AND METHODS

2.1. Materials

The paints evaluated in this study were produced with granite and marble waste (pigments), water (solvent), PVA resin (binder), biocidal (BAC Preservative, based on Isothiazolinones and Semi Acetal) and dispersant (WANPEX 1450, composed of Polyacrylic Acid Sodium Salt) additives.

The granite and marble wastes underwent an initial treatment to disaggregate and disperse the particles using a mechanical agitator. In addition, they were sieved through an ASTM 400 mesh sieve (0.037 mm opening). After this treatment, the granite waste exhibited a specific gravity of 2.60 g/cm³, according to NBR16605 (ABNT, 2017), and a specific surface area by the BET method of 6.11 m²/g. The marble waste showed a specific gravity of 2.82 g/cm³ and a specific surface area of 4.42 m²/g, using the same methodologies. Figure 3.1 illustrates the particle size distribution curves of the granite and marble waste obtained through the Bettersize laser granulometer. X-ray Fluorescence (XRF) analyses (Table 3.1) were obtained from a Shimadzu Micro-EDX-1300 spectrometer, indicating that the granite waste was primarily composed of SiO_2, while the marble waste consists predominantly of CaO. Mineralogical characterization through X-ray Diffraction (XRD) was performed in a D8 Discover diffractometer (Bruker), using CuKα radiation (1.5418 Å). This analysis revealed that the granite waste (Figure 3.2a) exhibited prominent peaks of quartz (SiO_2) and albite ($NaAlSi_3O_8$). Conversely, the marble waste (Figure 3.2b) showed stronger peaks of calcite ($CaCO_3$) and dolomite ($CaMg(CO_3)_2$).

Figure 3.1- Particle size distribution curves of granite waste and marble waste pigments.

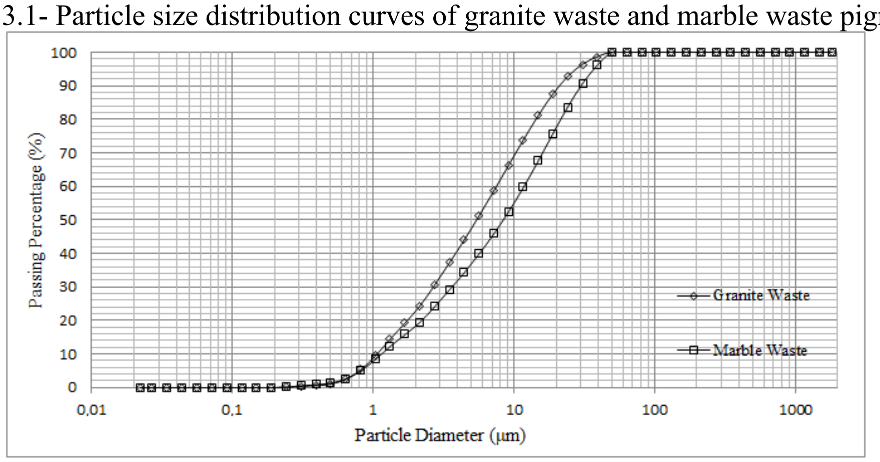
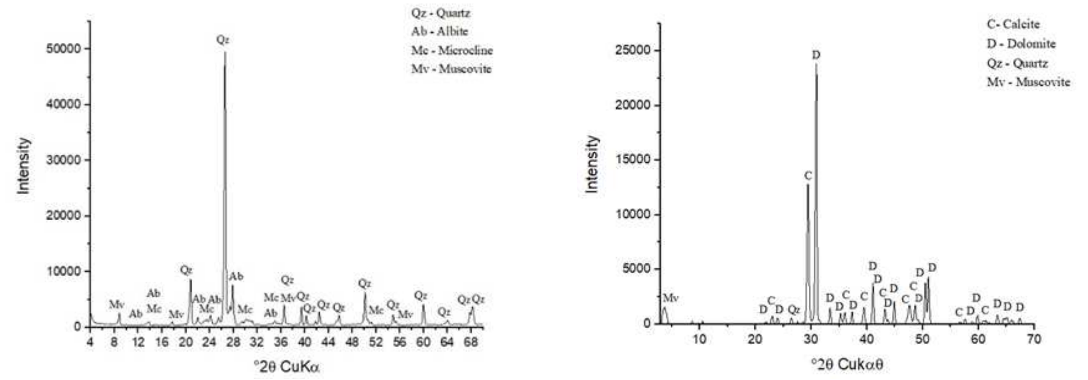


Table 3.1- XRF analysis of granite and marble waste pigments.

Pigment	SiO_2	Al_2O_3	K_2O	MgO	CaO	Na_2O	Fe_2O_3	SO_3	Others
Granite Waste	84.62	8.60	2.67	1.29	1.00	0.94	0.41	-	0.47
Marble Waste	4.91	-	1.02	16.68	76.59	-	-	0.77	0.03

Figure 3.2- XRD analysis: (a) granite waste pigment; (b) marble waste pigment.



(a) (b)

2.2. Paint production

A quaternary mixture design was selected for this study, with contents of granite and marble waste ranging from 0 to 100%; biocide ranging from 0 to 1.00%; and dispersant ranging from 0 to 4.00%. The ranges for additive variations were determined based on the maximum specifications recommended by manufacturers, in terms of the total paint mass.

Water was added to each mixture to achieve a consistent kinematic viscosity, resulting in a flow time of 23±1 seconds in the Ford cup viscometer with orifice number 4. Additionally, the resin content was maintained at 50% of the pigment mass, according to Lopes *et al.* (2024).

Table 3.2 presents the formulations of each paint sample prepared with granite and/or marble waste, both with and without biocidal and dispersant additives.

To produce the paints, pigments from granite and/or marble residues were dispersed in water and combined with biocide and/or dispersant additives, according to the proportions presented in Table 3.2. Mixing was done using a mechanical stirrer and a Cowles disk at 600 rpm for 10 minutes. Then, the PVA resin was added and mixed for another 10 minutes at 300 rpm.

Table 3.2- Mass of the paint components produced in this research.

SAMPLE	GW (g)	MW (g)	WATER (g)	RESIN (g)	BIOC. (g)	DISP. (g)
GW	500.00		377.42	250.00		
GW+B_{MED}	500.00		376.20	250.00	2.51	
GW+B_{MAX}	500.00		370.13	250.00	5.05	
GW+D_{MED}	500.00		362.81	250.00		10.20
GW+D_{MAX}	500.00		358.63	250.00		20.83
GW+B_{MED}+D_{MED}	500.00		355.63	250.00	2.56	10.26
GW+B_{MAX}+D_{MED}	500.00		354.43	250.00	5.15	10.31
GW+B_{MED}+D_{MAX}	500.00		351.37	250.00	2.62	20.94
GW+B_{MAX}+D_{MAX}	500.00		355.22	250.00	5.26	21.05
MW		500.00	335.13	250.00		
MW+B_{MED}		500.00	364.80	250.00	2.51	
MW+B_{MAX}		500.00	330.50	250.00	5.05	
MW+D_{MED}		500.00	268.09	250.00		10.20
MW+D_{MAX}		500.00	255.31	250.00		20.83
MW+B_{MED}+D_{MED}		500.00	260.69	250.00	2.56	10.26
MW+B_{MAX}+D_{MED}		500.00	259.37	250.00	5.15	10.31
MW+B_{MED}+D_{MAX}		500.00	249.30	250.00	2.62	20.94
MW+B_{MAX}+D_{MAX}		500.00	247.40	250.00	5.26	21.05
GW+MW	250.00	250.00	367.44	250.00		
GW+MW+B_{MED}	250.00	250.00	337.90	250.00	2.51	
GW+MW+B_{MAX}	250.00	250.00	315.02	250.00	5.05	
GW+MW+D_{MED}	250.00	250.00	269.78	250.00		10.20
GW+MW+D_{MAX}	250.00	250.00	253.57	250.00		20.83
GW+MW+B_{MED}+D_{MED}	250.00	250.00	289.00	250.00	2.56	10.26
GW+MW+B_{MAX}+D_{MED}	250.00	250.00	268.85	250.00	5.15	10.31
GW+MW+B_{MED}+D_{MAX}	250.00	250.00	288.65	250.00	2.62	20.94
GW+MW+B_{MAX}+D_{MAX}	250.00	250.00	284.91	250.00	5.26	21.05

Notes: GW: granite waste; MW: marble waste; BIOC.: biocidal additive; DISP.: dispersant additive; B_{MED}: biocidal additive added at a medium percentage to the mixture; B_{MAX}: biocidal additive added at maximum percentage to the mixture; D_{MED}: dispersant additive added at a medium percentage to the mixture; D_{MAX}: dispersant additive added at maximum percentage to the mixture.

2.3. Weathering resistance testing methodologies

2.3.1. Natural weathering

The natural weathering resistance test was conducted based on the specifications of G7 (ASTM, 2013), with appropriate adaptations.

Mortar plates were prepared to be used as the paint substrate, using cement, lime, and sand (mix proportion of 1:1:6, by volume). These plates had a surface area of 20x40 cm² and a thickness of 3.0 cm, simulating the external coating typically used in constructions. The 27 paint samples shown in Table 3.2 and an additional 8 samples of commercial paints (designated from A to H) were applied to the mortar plates to cover half of its total surface area. Three paint layers were applied, according to the specifications of the manufacturers of economic latex paints, and two plates were painted for each sample.

These boards were randomly fixed on a wooden structure (Figure 3.3a) that was properly oriented to the north at an angle of 20° relative to the vertical plane, as the municipality of Viçosa (Minas Gerais) is located at a latitude of 20º 45′ 14″ S. Thus, the paint films were exposed to maximum radiation incidence. Finally, the properly painted mortar plates were partially covered with a metal sheet (Figure 3.3b), so that only half of the dry paint film was exposed to the weathering. The paints were exposed to natural weathering for 12 months.

Figure 3.3- Weathering resistance test of paint samples: a) before fixing the metal sheet; b) after fixing the metal sheet.

(a)

(b)

2.3.2. Accelerated weathering

The accelerated weathering resistance test was conducted using a weathering chamber (Figures 3.4 and 3.5), designed based on the specifications of NBR 15380 (ABNT, 2015) and D 4587 (ASTM, 2019), with necessary adaptations. The exposure cycles selected for the present study consisted of 8 hours of UV exposure (UVA-340 lamp) at a temperature of (60±3) °C (Electrical heating), followed by 4 hours of condensation at a temperature of (50±3) °C (Boiler). The distance between the lamps and the samples was designed to achieve an irradiance of 0.77 $W/m^2/nm$.

The substrates of the paint samples were the mortar plates described in section 2.3.1, which were cut into fractions with a surface area of 10x10 cm² and a thickness of 3.0 cm. Only the paints with extreme contents of biocidal and/or dispersant additives, as well as the best-performing commercial paint, were evaluated. Three layers of paint were applied to each fractionated mortar plates. Three plates were painted for each sample, with one of them being protected from the weathering process.

Two plates of each sample were randomly placed inside the chamber and exposed to repetitive cycles of exposure to light, temperature, and humidity under controlled environmental conditions. Since the paints were applied on a cementitious substrate, the test lasted for 600 hours of exposure, with evaluations conducted every (200±10) hours.

Figure 3.4- Schematic representation of the accelerated weathering chamber (front view), dimensions in millimeters.

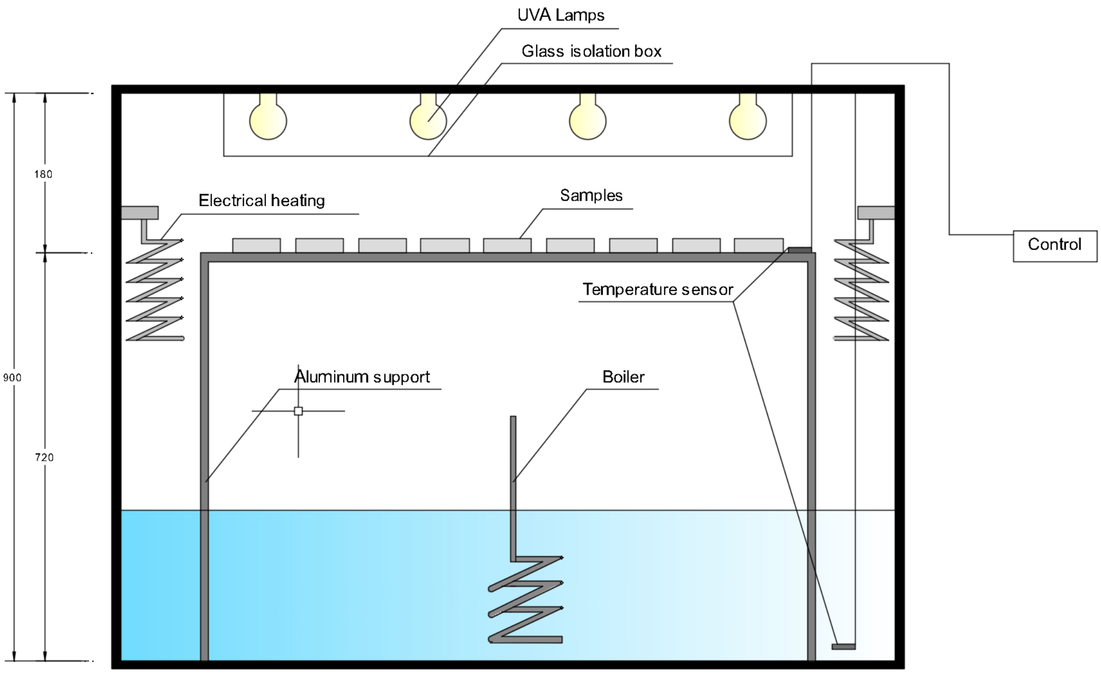


Figure 3.5- Accelerated weathering resistance test of paint samples.

2.4. Assessment of paints exposed to weathering

During the weathering tests, the samples were monitored monthly for natural weathering and every 200 hours for accelerated weathering. Prior to analysis, the boards were cleaned with a soft-bristled brush to remove dust. This monitoring involved visual inspection and image recording to identify the emergence and progression of pathological manifestations on the paint films, such as cracking and peeling. Photographic records were made using the same equipment and lighting conditions, creating a consistent standard for analysis.

The observed changes were correlated with temperature, sunlight exposure, and precipitation data obtained from the Viçosa Main Climatological Station (for natural weathering) and defined parameters of the exposure cycles (for the weathering chamber). Additionally, comparisons were made between the weathered paints and paints protected from the weathering process by determining the color difference using the delta-E method.

To evaluate the color change, the color was determined through the RGB system at 20 randomly selected points on the protected part and 20 points on the exposed part. Values that showed significant deviation from the mean were discarded.

The delta-E method quantitatively measures the difference between two colors in the CIELAB system. Delta-E values range from 0 to 100. This method is endorsed by the International Commission on Illumination (CIE) as it best represents the human color perception (BALDEVBHAI; ANAND, 2012; GALVÃO *et al.,* 2017). Delta-E was calculated by comparing the protected paint film with the weathered paint film using the Delta-E Calculator software (COLORMINE, 2024).

After 12 months, microscopic images were obtained to record the appearance of the paint films and their pathological manifestations using a Professional Technical 1600x Zoom USB Digital Microscope.

Pull-off tests were also conducted on all samples after the weathering tests to compare the protected and weather-exposed areas. A paint adhesion pull-off gauge was used in these tests, following the recommendations of the D4541 (ASTM, 2017) and ISO 4624 (ISO, 2016) standards.

2.5. Statistical analysis

The results of paint performance tests were used to create polynomial models that describe delta-E as a function of the independent variables of the mixture design. Additionally, an analysis of variance (ANOVA) was conducted to assess significant differences in the treatments with biocide and dispersant. To validate the ANOVA results, the homogeneity of variances between treatments and the normality of residuals were verified. Finally, the Tukey test was used to compare and identify the means that showed significant differences between the treatments, considering a confidence interval of 95%.

Furthermore, to correlate the Delta E values of natural and accelerated weathering, accelerated weathering trend lines were determined. With this, the number of days in the accelerated weathering chamber necessary to obtain the same deterioration observed in natural weathering was established. Then, a graphic correlation was carried out between the data from the two types of weathering. From this analysis, an equation was generated that describes the number of days in the accelerated weathering chamber to simulate the degradation of natural weathering, considering the specific conditions adopted in this study.

3. RESULTS AND DISCUSSION

Table 3.3 presents the meteorological data recorded by the Viçosa Conventional Station, including temperature, humidity, radiation, and precipitation data that represent the conditions experienced by the paint samples during the natural weathering test. Viçosa, like most Brazilian cities, has a tropical climate characterized by high average temperatures throughout the year and a narrow annual temperature range. Additionally, there are two well-defined seasons: one with high temperatures and significant precipitation, and another with moderate temperatures and little to no precipitation (LACERDA *et al.*, 2022; SANCHES; FIALHO; QUINA, 2017). Therefore, the paint samples subjected to natural weathering were analyzed at three time points: after 4 months of exposure (during the rainy season with high temperatures), 8 months (during the dry season with average temperatures), and 12 months (another rainy season with high temperatures).

Table 3.3- Meteorological data recorded by the Viçosa Conventional Station in the year 2023.

Month	Temperature (ºC)		Humidity (%)		Radiation (kJ.m^2)		Precipitation (mm)
	Average	Maximum	Average	Maximum	Average	Maximum	
January	22	30	85	98	1226	3664	404
February	23	33	82	98	1478	3830	144
March	23	31	82	98	1488	3608	127
April	21	31	84	98	1153	3631	89
May	18	28	85	99	1122	2903	7
June	16	27	84	99	1069	2804	6
July	17	29	82	99	1055	2749	29
August	19	31	82	99	1130	3035	5
September	21	37	76	98	1270	3447	73
October	23	35	79	97	1182	3779	129
November	24	37	74	98	1623	3751	106
December	24	35	78	98	1400	3905	48

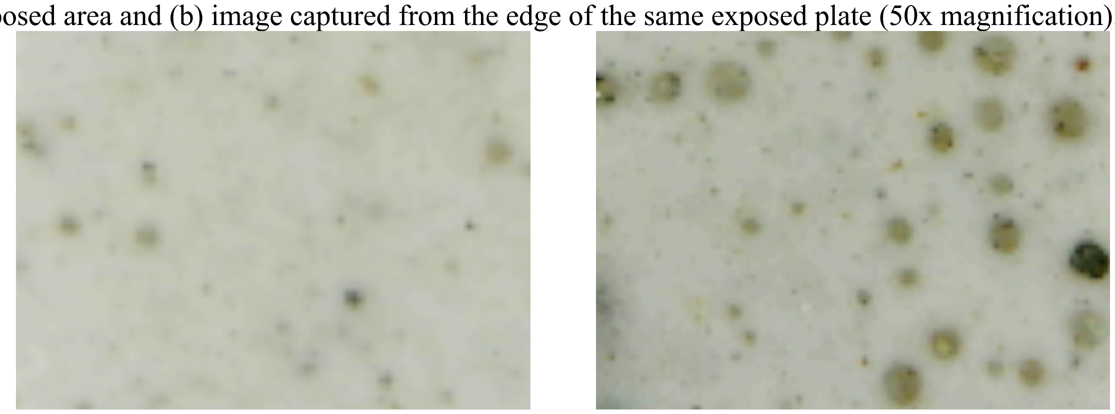
In the accelerated weathering tests, the three cycles reached a maximum temperature of 63 °C and an average temperature of 53 °C. Furthermore, the samples exposed to natural weathering were positioned almost vertically (at a slight incline of 20º from the vertical), while the samples exposed to accelerated weathering were positioned horizontally, receiving maximum radiation for prolonged periods. Therefore, the conditions in accelerated weathering were more severe and contributed to a greater deterioration of the paints.

Figure 3.6 presents images of the mortar plates painted with samples of paints containing granite and marble waste, as well as commercial paints, after twelve months of exposure to natural weathering. Noticeable color differences were observed between the protected parts and the parts exposed to weathering. Furthermore, this color variation appeared to be non-uniform. This occurred because the metal sheet did not fully protect the paint film, which was exposed to diffuse light, high temperatures, and humidity. This effect was especially pronounced in areas of direct contact between the sheet metal and the paint film. Additionally, the metal sheet fold designed to collect rainwater could shade the upper part of the paint film. Other studies, such as those by Andrady et al. (2023) and Masuda et al. (2019), have also identified this non-uniform color variation in samples of polymeric materials subjected to natural weathering. According to Kumar et al. (2021), the location and method of installation of modules, particularly their tilt angle, can influence the level of UV irradiance received by the module.

Figure 3.6- Paints exposed to the natural weathering resistance test for twelve months.

Figure 3.7 presents microscope images obtained from a paint sample, evidencing the typical color differences identified in paint films subjected to natural weathering. These differences revealed a greater growth of biological agents at some points of the specimens. According to Gaylarde *et al.* (2011), microbial development can occur through constituents of the coating itself, as well as through the action of rain and wind, which can transport small plant or animal fragments, spores, microbial cells, as well as minerals and atmospheric pollutants. In this case, hygrothermal conditions are particularly relevant, with high humidity or condensation, combined with elevated temperatures, favoring microbial growth (CARPINO *et al*., 2023; DU; LI; YU, 2021).

Figure 3.7- Paint films exposed to natural weathering: (a) image captured from the central part of the exposed area and (b) image captured from the edge of the same exposed plate (50x magnification).



(a) (b)

Table 3.4 presents the color change results, based on values of delta-E obtained from comparisons between the protected paint films and the exposed elements. This Table also presents the pathological manifestations identified in the paint samples and the pull-off strength of the paint films. The samples did not exhibit cracks or peeling, indicating that the paints effectively resisted temperature variations and intense rains. Additionally, the PVA resin content used to produce the samples was adequate to form a paint film and ensure its adherence to the substrate.

Table 3.4- Performance results of samples exposed to natural weathering.

Sample	Color change (delta-E)			Cracks or peeling	Pull-off strength (MPa) - 12 months		
	4 months	8 months	12 months		Protected specimen	Exposed specimen	Failure mode
GW	2.1	3.6	4.6	-	0.50	0.60	Failure in the mortar
GW+B_{MED}	1.7	3.2	4.3	-	0.60	0.65	Failure in the mortar
GW+B_{MAX}	1.9	2.8	3.9	-	0.60	0.70	Failure in the mortar
GW+D_{MED}	3.5	5.2	7.1	-	0.55	0.60	Failure in the mortar
GW+D_{MAX}	3.9	4.5	7.2	-	0.50	0.65	Failure in the mortar
GW+B_{MED}+D_{MED}	3.1	4.7	7.1	-	0.70	1.00	Failure in the mortar
GW+B_{MAX}+D_{MED}	2.7	3.9	6.7	-	0.90	0.95	Failure in the mortar
GW+B_{MED}+D_{MAX}	4.1	5.0	8.9	-	0.65	0.60	Failure in the mortar
GW+B_{MAX}+D_{MAX}	3.8	6.4	8.1	-	0.70	0.55	Failure in the mortar
MW	4.1	6.3	9.2	-	0.70	0.95	Failure in the mortar
MW+B_{MED}	3.8	5.5	7.6	-	0.95	0.80	Failure in the mortar
MW+B_{MAX}	3.2	4.9	5.9	-	0.60	0.90	Failure in the mortar
MW+D_{MED}	4.5	7.5	9.4	-	0.70	0.90	Failure in the mortar
MW+D_{MAX}	4.8	7.3	10.1	-	0.90	1.00	Failure in the mortar
MW+B_{MED}+D_{MED}	4.2	6.4	8.3	-	0.90	0.85	Failure in the mortar
MW+B_{MAX}+D_{MED}	3.9	5.6	7.3	-	0.55	0.80	Failure in the mortar
MW+B_{MED}+D_{MAX}	4.1	6.6	9.3	-	0.60	0.80	Failure in the mortar
MW+B_{MAX}+D_{MAX}	3.9	5.8	8.1	-	0.80	0.50	Failure in the mortar
GW+MW	3.2	5.3	7.3	-	0.60	0.80	Failure in the mortar
GW+MW+B_{MED}	3.1	4.8	7.1	-	0.80	0.90	Failure in the mortar
GW+MW+B_{MAX}	2.2	4.3	6.2	-	0.80	0.75	Failure in the mortar

GW+MW+D_{MED}	3.8	5.2	7.8	-	0.80	0.90	Failure in the mortar
GW+MW+D_{MAX}	4.3	6.4	8.1	-	0.60	0.60	Failure in the mortar
GW+MW+B_{MED}+D_{MED}	3.4	5.0	7.3	-	0.80	0.70	Failure in the mortar
GW+MW+B_{MAX}+D_{MED}	3.1	4.6	6.9	-	0.85	0.60	Failure in the mortar
GW+MW+B_{MED}+D_{MAX}	3.8	6.7	8.0	-	1.00	0.80	Failure in the mortar
GW+MW+B_{MAX}+D_{MAX}	3.5	6.2	7.7	-	0.95	0.80	Failure in the mortar

The pull-off strength of all samples ranged from 0.5 to 1.0 MPa. Moreover, all ruptures occurred in the mortar layer, indicating good adhesion between the paint and the substrate. The two-sample t-test revealed that the average strength in protected samples was 0.722 MPa. In samples exposed to weathering, it was 0.765 MPa, with a standard deviation of 0.146 MPa. This statistical analysis indicate that there is no significant difference in the averages obtained for the protected and exposed areas. According to NBR 13749 (2013), the pull-off strength for exterior wall coatings should exceed 0.3 MPa at the age of 28 days. This underscores the compatibility of the obtained results with expectations for a mortar that has been cured for over a year. According to Saraswathy and Rengaswamy (1998), painting on a cementitious substrate promotes an adhesion resistance greater than the surface resistance of the substrate, although the values are in the same range. The cement substrate is heterogeneous and significantly porous. Hence, the durability of any surface coating is related especially to the adhesion between the surface coating and the cement substrate (COFFETTI *et al.*, 2021).

The paints containing granite waste exhibited low values of delta-E over the 12-month period. The lower the delta-E, the less overall color modification occurs in the coatings. Therefore, paints produced with granite waste are more color-stable than those produced with marble waste. This may be attributed to the high percentage of silica present in the material, which is responsible for making the paint films more resistant and durable. Several studies demonstrated that adding silica particles to paint formulations, especially nanoparticles, causes improvements in the resistance, hydrophobic surface properties, and adhesion to cementitious substrates (AHMED; MOHAMED; ABD EL-GAWAD, 2018; DIEBOLD *et al.*, 2022; NADERIZADEH; ATHANASSIOU; BAYER, 2018). Furthermore, the granite waste has a smaller particle size and a larger specific surface area than the marble waste. According to Królikowska, Komorowski and Bonora (2021), the size of the particles and their wettability by the binder influence the durability and efficiency of the coating. Smaller particles tend to create a more compact protective layer.

Furthermore, the presence of the biocidal additive reduced the delta-E, while the dispersant additive increased the color difference between the protected parts and those exposed to weathering (Figure 3.8). The Tukey test results suggested that the means obtained at different concentrations of biocide were equal, indicating that the biocide had no significant effect on the delta-E parameter, contrary to what happened with the dispersant. In addition to biological agents' growth that can change the color of paint films, Diebold et al. (2022) state that the durability of the paint film is primarily determined by the resistance of the resin to degradation caused by exposure to solar radiation. Therefore, the dispersant additive probably affected the resin's sensitivity to radiation and/or the growth of biological agents. According to Novak and Ormsby (2023), the additives in vinyl paints can influence the final properties and the ageing behavior of the products, even for low concentrations, generally below 5%. To date, there has been limited research on the effects of various additives on the properties of poly(vinyl acetate) paints. It is presumed that the photochemical degradation of poly(vinyl acetate) causes physical changes in the material, such as color changes (yellowing and loss of transparency), loss of mechanical properties, and/or favoring the growth of biological agents (NOVAK; ORMSBY, 2023).

Figure 3.8- Contour plot of delta-E (exposure of 12 months) versus contents of biocide and dispersant additives.

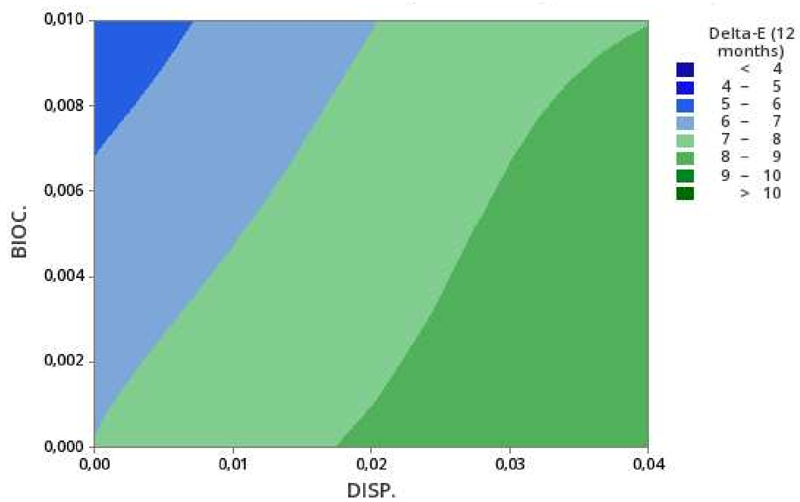


Table 3.5 presents microscope images of paints containing marble waste that experienced the most significant color variation. Paints with higher contents of dispersants exhibited greater damage, while paints with higher levels of biocide exhibited less color alteration. The darker color observed in the microscope images of the exposed paints may be

related to bacterial growth, as well as the removal of the paint by the effects of rain and exposure of the substrate.

Table 3.5- Comparison between exposed and protected samples of different paints (magnification of 50x).

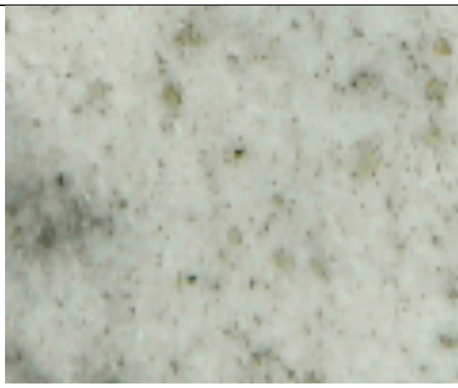
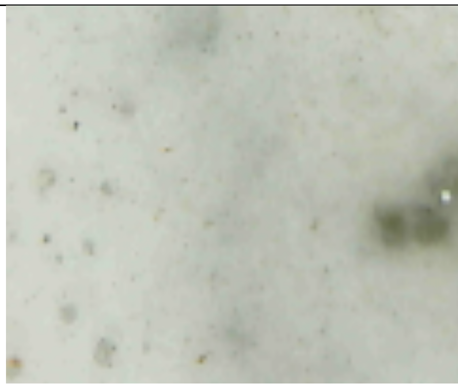
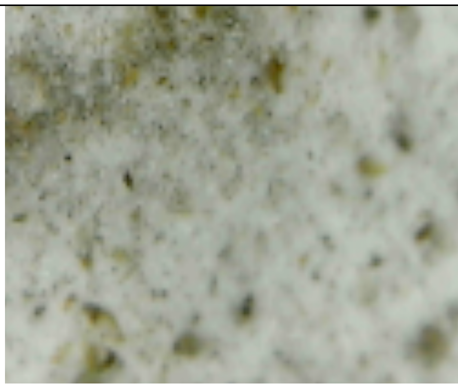
Sample	Exposed specimen	Protected specimen
MW		
MW+$B_{MAX.}$		
MW+$D_{MAX.}$		

Table 3.6 shows the performance of commercial paints under natural weathering conditions. No significant difference was observed between the pull-off strength values of paints containing granite and marble waste and those of commercial paints, due to the use of the same substrate. Figure 3.9 illustrates a comparison of the delta-E values of paints exposed

to natural weathering for 12 months. It is noteworthy that only two commercial paints exhibited a minimal color variation over time (less than 2). A delta-E close to 2 is considered favorable, indicating a small color difference (KARMA, 2020). Conversely, the other commercial paints perform similarly to granite waste paints without dispersants. It is important to highlight that the commercial paints were produced with acrylic resin, while the paints produced in this study had polyvinyl acetate resin. According to Diebold (2020), the susceptibility of a resin to direct degradation is determined by its chemistry. Resins are categorized into low durability and high durability classes. Paints derived from polyvinyl acetate are highly sensitive to changes in color and gloss when exposed to light, are vulnerable to various solvents and are less resistant to attack by biological agents. The photodegradation mechanism of vinyl acetate pigmented paints can cause a visible color change (NOVAK; ORMSBY, 2023).

Table 3.6- Performance results of commercial paints exposed to natural weathering.

Sample	Color change (delta-E)			Cracks or peeling	Pull-off strength (MPa) - 12 months		
	4 months	8 months	12 months		Protected specimen	Exposed specimen	Failure mode
A	1.2	2.7	4.0	-	0.80	0.80	Failure in the mortar
B	4.0	5.2	6.8	-	0.50	0.70	Failure in the mortar
C	2.8	4.1	5.2	-	0.60	0.70	Failure in the mortar
D	2.8	4.8	5.7	-	0.80	0.70	Failure in the mortar
E	2.3	3.9	4.8	-	0.80	0.65	Failure in the mortar
F	1.2	2.0	3.7	-	0.60	0.50	Failure in the mortar
G	0.8	1.2	1.9	-	0.70	0.60	Failure in the mortar
H	0.3	0.6	1.1	-	0.70	0.60	Failure in the mortar

In accelerated weathering, the average pull-off strength of the protected samples was 0.700 MPa, while the average strength of the exposed samples was 0.662 MPa. The values obtained in the accelerated weathering tests were very close to those obtained in natural weathering tests, indicating that the paint films exhibited good adhesion to the substrate and that the observed values were related to the pull-off strength of the mortar.

Table 3.7 presents the color change results, in terms of delta-E values obtained from comparisons between the protected paint films and paint films exposed to accelerated weathering. Furthermore, this table also presents the trend line equation for the Delta E values obtained for each mixture. It is observed that the coefficients obtained for the granite and/or marble residue paints are very similar, while the coefficient for the commercial paint (H) is significantly lower, indicating a lower level of color alteration in the commercial paint.

Additionally, the R^2 values, all above 0.95, demonstrate that the equations accurately describe the experimental values. A linear degradation is observed in the paint films within the accelerated weathering chamber.

Figure 3.9- Comparison of delta-E at 12 months for granite and marble waste paints versus commercial paints.

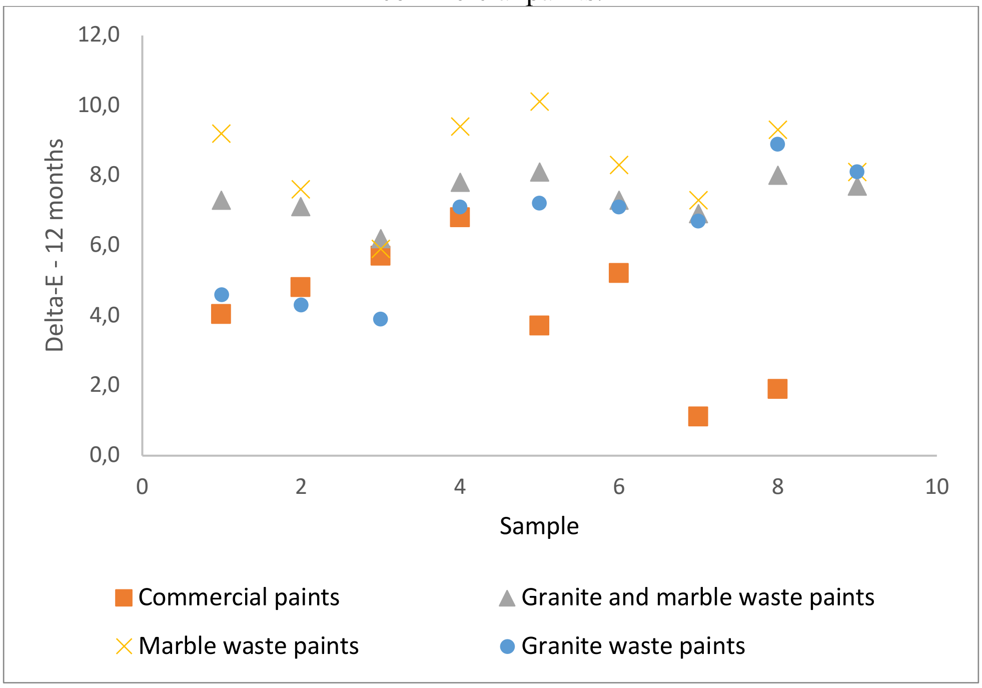


Table 3.7 - Performance results of samples exposed to accelerated weathering.

Sample	Color change (delta-E)			Tendency line		Cracks or peeling
	Cycle 1	Cycle 2	Cycle 3	Equation	R^2	
GW	3.4	5.1	7.6	y= 0.3250x	0.99	-
GW+Bmax	2.8	4.5	5.9	y=0.2634x	0.99	-
GW+Dmax	4.2	6.9	8.9	y=0.3995x	0.99	-
GW+Bmax+Dmax	5.6	7.9	10.1	y=0.4616x	0.98	-
MW	4.8	8.6	12.6	y=0.5339x	0.99	-
MW+Bmax	4.5	6.5	7.94	y=0.3693x	0.97	-
MW+Dmax	7.4	11.5	12.23	y=0.5997x	0.95	-
MW+Bmax+Dmax	5.5	9.1	13.06	y=0.5614x	0.99	-
GW+MW	4.1	7.7	10.04	y=0.4430x	0.99	-
GW+MW+Bmax	3.8	7.1	9.5	y=0.4152x	0.99	-
GW+MW+Dmax	4.5	7.9	10.04	y=0.4500x	0.99	-
GW+MW+Bmax+Dmax	4.0	7.4	9.7	y=0.4277x	0.99	-
H	0.8	1.3	1.9	y=0.0815x	0.99	-

Figure 3.10 illustrates a comparison of delta-E results obtained from different paint samples exposed to natural weathering (4 and 8 months) and accelerated weathering (Cycle 1). After just one cycle (8.33 days) of accelerated weathering, the paint deterioration degree surpassed that observed in samples exposed to natural weathering for 4 months. Figure 3.11 compares delta-E results of paint samples subjected to natural weathering (12 months) and accelerated weathering (Cycle 2 and Cycle 3). After only three cycles (25 days) of accelerated weathering, the paint deterioration degree exceeded that observed in samples subjected to natural weathering for 12 months. These findings underscore the efficiency and rapidity of the accelerated weathering method in simulating extreme exposure conditions and predicting material performance under such circumstances.

Table 3.8 presents polynomials described as functions of the independent variables of the experimental mixing design, considering the significance between interactions for p-value<0.05. These equations confirmed the previous discussions: marble waste caused greater paint color changes than granite waste; the dispersant additive positively affected the delta-E increase, unlike the biocide additive; the third cycle procedures yielded higher delta-E values than natural exposure for 12 months.

Figure 3.10- Comparison of delta-E values obtained in samples subjected to natural weathering (NW- 4 months and 8 months) and accelerated weathering (AW- Cycle 1) tests.

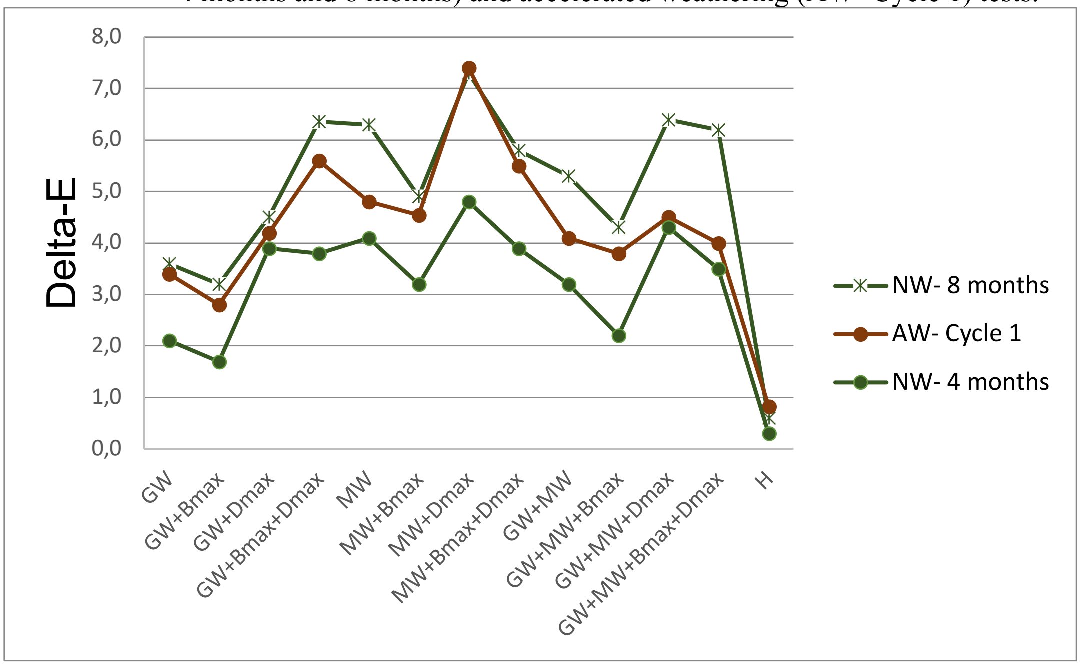


Figure 3.11- Comparison of delta-E values obtained in samples subjected to natural weathering (NW-12 months) and accelerated weathering (AW- Cycles 2 and 3) tests.

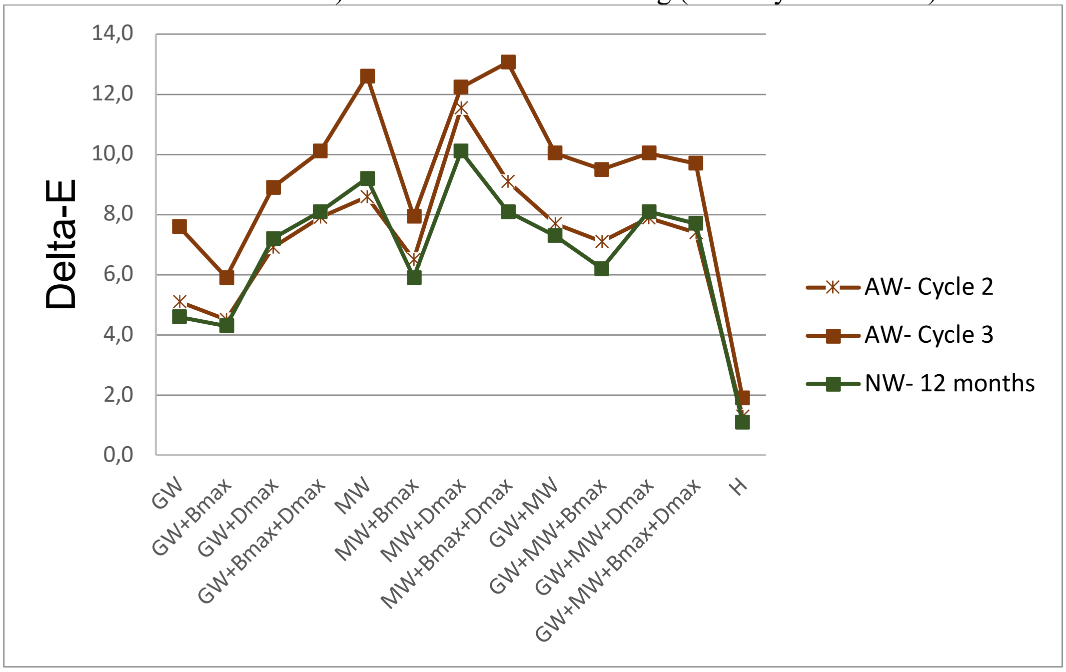


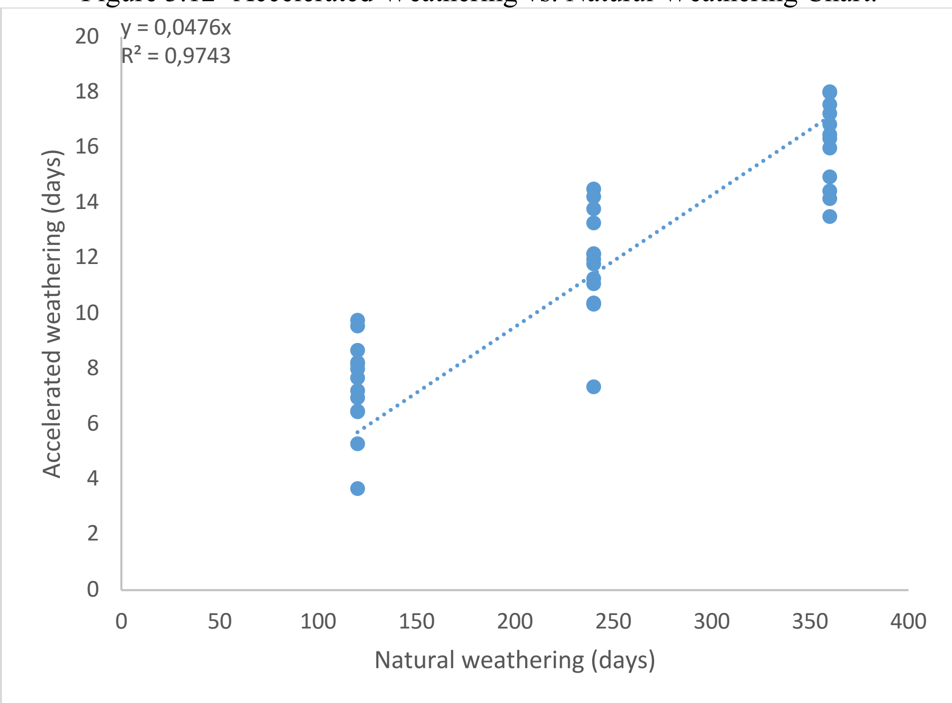
Table 3.8- Delta-E (DE) polynomial models for paints containing granite and marble waste pigments.

Regression equations	**R^2**
DE (4 months)= 2.3a + 4.1b – 63.1c + 16.0d + 36.6ad	93.8%
DE (8 months)= 4.0a + 5.9b – 70.6c + 44.4d	79.2%
DE (12 months)= 4.7a + 9.0b – 220.9c + 35.2d + 241.6ab + 54.7ad	88.3%
DE (Cycle 1)= 3.3a + 4.8b – 31.0c + 49.1d	80.8%
DE (Cycle 2)= 5.2a + 8.1b – 95.8c + 73.6d	89.9%
DE (Cycle 3)= 7.3a + 10.8b – 98.0c + 73.4d	77.0%

Note: a- granite waste; b- marble waste; c- biocide additive; d- dispersant additive.

Figure 3.12 graphically illustrates the correlation between natural and accelerated weathering. The trend line equation indicates that 365 days of natural weathering in the city of Viçosa can be replicated in just 17 days in the accelerated weathering chamber. Moreover, the R^2 value of 0.97 demonstrates the precision of the equation based on the experimental results obtained. Studies comparing natural weathering with accelerated weathering have also noted that accelerated weathering led to higher paint deterioration (CARMONA-QUIROGA *et al.*, 2017; COGULET; BLANCHET; LANDRY, 2019; CRISTOFORETTI *et al.*, 2023; LANKONE *et al.*, 2020). This is because accelerated exposure provides severe climatic conditions, often harsher than those found in the final end-use environment, and therefore can lead to degradation that would never occur in service conditions (COGULET; BLANCHET; LANDRY, 2019). Carmona-Quiroga *et al.* (2017) observed that 83.3 days of accelerated weathering in a QUV chamber surpassed 1 year of natural exposure in a maritime temperate climate in southern England. Frigione and Rodriguez-Pietro (2021) replicated aging effects due to one year of natural exposure of polymers with about 25 days of accelerated UV exposure. Cao *et al.* (2015) found that 32 days of accelerated xenon lamp aging is equivalent to one year of natural weathering on cool pavement coatings. Xie *et al.* (2020) observed that 18 days of laboratory accelerated exposure were required to simulate a 25-year real-world condition of coatings for cool pavements. According to Cogulet, Blanchet, and Landry (2019), the results provided by accelerated weathering tests should always be interpreted with caution to avoid misleading conclusions. Accelerated weathering only provides an indication of the likely performance of the paint. The greater the deviation of the exposure testing method from the service exposure parameters, the less accurate the durability prediction becomes.

Figure 3.12- Accelerated Weathering vs. Natural Weathering Chart.



4. CONCLUSION

In conclusion, this study provided new and important insights into the following aspects:

- The study revealed the viability of producing sustainable and low-cost paints using marble waste and, mainly, granite waste. These paints demonstrated good adhesion to the mortar substrate and resistance to weathering.

- The presence of biocidal additives in PVA latex paints had no significant effect on weathering resistance. However, the presence of dispersant additives in PVA latex paints contributed to increased paint color variation over time, providing valuable insights for the development of more resistant paint formulations.
- Paints containing granite waste exhibited deterioration levels compatible with commercial paints.
- 12 months of natural weathering were reproduced in approximately 17 days of accelerated weathering. The rapid deterioration observed in accelerated weathering reinforces the effectiveness of this method in simulating extreme conditions, allowing the performance of paints to be predicted over time.

These conclusions highlight the importance of the present study in the search for more sustainable solutions in the construction sector, contributing to the development of more eco-friendly materials.

REFERENCES

ABRAFATI. **O Setor de Tintas no Brasil.** 2022. Available at: https://abrafati.com.br/setor-de-tintas/dados-do-setor/.

AHMED, N. M.; MOHAMED, M. G.; ABD EL-GAWAD, W. M. Corrosion protection performance of silica fume waste-phosphates core-shell pigments. **Pigment & Resin Technology**, vol. 47, no. 3, p. 261–271, 8 May 2018. https://doi.org/10.1108/PRT-07-2017-0069.

AJIBOYE, T. O.; OYEWO, O. A.; ONWUDIWE, D. C. Simultaneous removal of organics and heavy metals from industrial wastewater: A review. **Chemosphere**, vol. 262, p. 128379, Jan. 2021. https://doi.org/10.1016/j.chemosphere.2020.128379.

ALLEN, N. S.; MCINTYRE, R.; KERROD, J. M.; HILL, C.; EDGE, M. Photo-Stabilisation and UV Blocking Efficacy of Coated Macro and Nano-Rutile Titanium Dioxide Particles in Paints and Coatings. **Journal of Polymers and the Environment**, vol. 26, no. 11, p. 4243–4257, 2018. DOI 10.1007/s10924-018-1298-0.

ALMADA, B. S.; MELO, L. de S.; SILVA, G. J. B.; SANTOS, W. J. dos; AGUILAR, M. T. P. Effect of the waste ornamental rocks on the hydration and life cycle of Portland cement composites. **Construction and Building Materials**, vol. 395, p. 132353, Sep. 2023. https://doi.org/10.1016/j.conbuildmat.2023.132353.

AMERICAN SOCIETY FOR TESTING MATERIALS. **ASTM G7**: Standard Practice for Atmospheric Environmental Exposure Testing of Nonmetallic Materials. ASTM International, West Conshohocken, PA, 2013.

AMERICAN SOCIETY FOR TESTING MATERIALS. **ASTM D 4541:** Standard Test Method for Pull-Off Strength of Coatings Using Portable Adhesion Testers. ASTM International, West Conshohocken, PA, 2022.

ANDRADY, A. L.; HEIKKILÄ, A. M.; PANDEY, K. K.; BRUCKMAN, L. S.; WHITE, C. C.; ZHU, M.; ZHU, L. Effects of UV radiation on natural and synthetic materials. **Photochemical & Photobiological Sciences**, vol. 22, no. 5, p. 1177–1202, 11 Apr. 2023.

ASSOCIAÇÃO BRASILEIRA DE NORMAS TÉCNICAS. **NBR 15380:** Tintas para construção civil — Método para avaliação de desempenho de tintas para edificações não industriais — Resistência à radiação UV e à condensação de água pelo ensaio acelerado. Rio de Janeiro, 2015.

ASSOCIAÇÃO BRASILEIRA DE NORMAS TÉCNICAS. **NBR 16605:** Cimento Portland e outros materiais em pó — Determinação da massa específica. Rio de Janeiro, 2017.

BALDEVBHAI, P. J.; ANAND, R. S. Color Image Segmentation for Medical Images using L*a*b* Color Space. **IOSR Journal of Electronics and Communication Engineering (IOSRJECE)**,vol. 1, n. 2, p. 24-45, 2012.

CAO, X.; TANG; B.; YUAN, Y.; ZOU, X. **Study on indoor and outdoor aging behaviors of heat-reflective coating for pavement in chongqing area**. China, in: Transp. Res. Board 94th Annu. Meet, 2015. https://trid.trb.org/view/1337390.

CARMONA-QUIROGA, P. M.; JACOBS, R. M. J.; MARTÍNEZ-RAMÍREZ, S.; VILES, H. A. Durability of anti-graffiti coatings on stone: natural vs accelerated weathering. **PLOS ONE**, vol. 12, no. 2, p. e0172347, 23 Feb. 2017. https://doi.org/10.1371/journal.pone.0172347.

COLORMINE. **Delta-E Calculator.** ColorMine.org, 2024.

CHUKWUMA, O. U.; UCHENNA, O. M.; OGONNA, U. S.; CHINEDU, O. S. Effects of Effluents' Discharge from Some Paint Industries on Soil's Physicochemical Properties and Bioattenuation of Polluted Soil. **Industrial and Domestic Waste Management**, vol. 2, no. 2, p. 46–60, 3 Oct. 2022. https://doi.org/10.53623/idwm.v2i2.110.

COFFETTI, D.; CROTTI, E.; GAZZANIGA, G.; GOTTARDO, R.; PASTORE, T.; COPPOLA, L. Protection of Concrete Structures: Performance Analysis of Different Commercial Products and Systems. **Materials**, vol. 14, no. 13, p. 3719, 2 Jul. 2021. https://doi.org/10.3390/ma14133719.

COGULET, A.; BLANCHET, P.; LANDRY, V. Evaluation of the Impacts of Four Weathering Methods on Two Acrylic Paints: Showcasing Distinctions and Particularities. **Coatings**, vol. 9, no. 2, p. 121, 15 Feb. 2019. DOI 10.3390/coatings9020121.

CRISTOFORETTI, A.; ROSSI, S.; DEFLORIAN, F.; FEDEL, M. Comparative study between natural and artificial weathering of acrylic-coated steel, aluminum, and galvanized steel. **Materials and Corrosion**, vol. 74, no. 10, p. 1429–1438, 12 Oct. 2023. https://doi.org/10.1002/maco.202313858.

DIEBOLD, M. P. Optimizing the benefits of TiO2 in paints. **Journal of Coatings Technology and Research**, vol. 17, no. 1, p. 1–17, 25 Jan. 2020. https://doi.org/10.1007/s11998-019-00295-2.

DIEBOLD, M.; BACKER, S. de; NIEDENZU, P. M.; HESTER, B. R.; VANHECKE, F. A. C. Durability of Paints, Plastics, and Paper Laminates. **Pigments, Extenders, and Particles in Surface Coatings and Plastics**. Cham: Springer International Publishing, 2022. p. 483–543. https://doi.org/10.1007/978-3-030-99083-1_14.

FAZENDA, J. M. R. **Paints: Science and Technology (in portuguese)**. [*S. l.*: *s. n.*], 2009.

FRIGIONE, M.; RODRÍGUEZ-PRIETO, A. Can Accelerated Aging Procedures Predict the Long Term Behavior of Polymers Exposed to Different Environments? **Polymers**, vol. 13, no. 16, p. 2688, 12 Aug. 2021. https://doi.org/10.3390/polym13162688.

GALVÃO, J. L. B.; ANDRADE, H. D.; BRIGOLINI, G. J.; PEIXOTO, R. A. F.; MENDES, J. C. Reuse of iron ore tailings from tailings dams as pigment for sustainable paints. **Journal of Cleaner Production**, vol. 200, p. 412–422, 2018. https://doi.org/10.1016/j.jclepro.2018.07.313.

GONZÁLEZ-LÓPEZ, M. E.; MARTÍN DEL CAMPO, A. S.; ROBLEDO-ORTÍZ, J. R.; ARELLANO, M.; PÉREZ-FONSECA, A. A. Accelerated weathering of poly(lactic acid) and its biocomposites: A review. **Polymer Degradation and Stability**, vol. 179, p. 109290, Sep. 2020. https://doi.org/10.1016/j.polymdegradstab.2020.109290.

KARMA, I. G. M. Determination and Measurement of Color Dissimilarity. **International Journal of Engineering and Emerging Technology**, vol. 5, no. 1, p. 67–71, 2020.

KRÓLIKOWSKA, A.; KOMOROWSKI, L.; BONORA, P. L. The effect of size and distribution of inert pigment on the performance of organic coatings. **Corrosion Engineering, Science and Technology**, vol. 56, no. 2, p. 137–143, 17 Feb. 2021. https://doi.org/10.1080/1478422X.2020.1824442.

KUMAR, S.; ALHAMADANI, H.; HASSAN, S.; ALHELOO, A.; HANIFI, H.; JOSEPH JOHN, J.; MATHIAK, G.; ALBERTS, V. Comparative Investigation and Analysis of Encapsulant Degradation and Glass Abrasion in Desert Exposed Photovoltaic Modules. 20 Jun. 2021. **2021 IEEE 48th Photovoltaic Specialists Conference (PVSC)** [...]. [*S. l.*]: IEEE, 20 Jun. 2021. p. 0793–0798. https://doi.org/10.1109/PVSC43889.2021.9519122.

LACERDA, M. S.; MARTINS, H. de S. R.; TEMOTEO, A. da S.; EMILIANO, P. C. Precipitation pattern in Viçosa-MG: a case study via time series. **Revista Agrogeoambiental**,, p. e20221642, 17 Oct. 2022. https://doi.org/10.18406/2316-1817v14n120221642.

LANKONE, R. S.; RUGGIERO, E.; GOODWIN, D. G.; VILSMEIER, K.; MUELLER, P.; PULBERE, S.; CHALLIS, K.; BI, Y.; WESTERHOFF, P.; RANVILLE, J.; FAIRBROTHER, D. H.; SUNG, L.-P.; WOHLLEBEN, W. Evaluating performance, degradation, and release behavior of a nanoform pigmented coating after natural and accelerated weathering. **NanoImpact**, vol. 17, p. 100199, Jan. 2020. https://doi.org/10.1016/j.impact.2019.100199.

LOPES, M. M. S.; ALVARENGA, R. de C. S. S.; PEDROTI, L. G.; RIBEIRO, J. C. L.; CARVALHO, A. F. de; CARDOSO, F. de P.; MENDES, B. C. Influence of the incorporation of granite waste on the hiding power and abrasion resistance of soil pigment-based paints. **Construction and Building Materials**, vol. 205, p. 463–474, 2019. https://doi.org/10.1016/j.conbuildmat.2019.02.046.

LOPES, M. M. S.; PEDROTI, L. G.; LIMA, G. E. S. de; RIBEIRO, J. C. L.; NALON, G. H.; MENDES, B. C.; OLIVEIRA, A. L. de. Influence of the Incorporation of Granite Waste on the Weathering Resistance of Soil Pigment-Based Paints. **Characterization of Minerals, Metals, and Materials 2021**. Springer. [*S. l.*: *s. n.*], 2021. p. 471–481. DOI 10.1007/978-3-030-65493-1_47.

LOPES, M. M. S.; PEDROTI, L. G.; OLIVEIRA, A. F. de; RIBEIRO, J. C. L.; CARVALHO, J. M. F. de; CARVALHO, A. F. de; CARDOSO, F. de P.; NALON, G. H.; LIMA, G. E. S. de. Optimization of performance of sustainable paints using granite waste through the variation of particle size and pH. **Journal of Cleaner Production**, vol. 326, p. 129418, Dec. 2021. DOI 10.1016/j.jclepro.2021.129418.

MANDAL, J.; YANG, Y.; YU, N.; RAMAN, A. P. Paints as a Scalable and Effective Radiative Cooling Technology for Buildings. **Joule**, vol. 4, no. 7, p. 1350–1356, Jul. 2020. DOI 10.1016/j.joule.2020.04.010.

MASUDA, K.; TSUCHIDA, K.; INOUE, T.; GILLIAM, M. A self-assembled, silicone acrylate coating formulation and detection of the optically non-uniform structure with reflectance spectroscopy. **Journal of Coatings Technology and Research**, vol. 16, no. 4, p. 923–931, 16 Jul. 2019. https://doi.org/10.1007/s11998-018-00171-5.

MOURA, H. R. de C. V.; PEDROTI, L. G.; LOPES, M. M. S.; CARVALHO, J. M. F. de; RIBEIRO, J. C. L.; DIAS, J. C. B. Influence of biocide and dispersant additives on the performance and durability of building paints produced with granite waste. **Construction and Building Materials**, vol. 409, p. 134112, Dec. 2023. https://doi.org/10.1016/j.conbuildmat.2023.134112.

NADERIZADEH, S.; ATHANASSIOU, A.; BAYER, I. S. Interfacing superhydrophobic silica nanoparticle films with graphene and thermoplastic polyurethane for wear/abrasion resistance. **Journal of Colloid and Interface Science**, vol. 519, p. 285–295, Jun. 2018. https://doi.org/10.1016/j.jcis.2018.02.065.

NAYAK, S. K.; SATAPATHY, A.; MANTRY, S. Use of waste marble and granite dust in structural applications: A review. **Journal of Building Engineering**, vol. 46, p. 103742, Apr. 2022. https://doi.org/10.1016/j.jobe.2021.103742.

NOVAK, M.; ORMSBY, B. Poly(Vinyl Acetate) Paints: A Literature Review of Material Properties, Ageing Characteristics, and Conservation Challenges. **Polymers**, vol. 15, no. 22, p. 4348, 7 Nov. 2023. https://doi.org/10.3390/polym15224348.

PEREIRA, M. M. L.; CAPUZZO, V. M. S.; LAMEIRAS, R. de M. Evaluation of use of marble and granite cutting waste to the production of self-compacting concrete. **Construction and Building Materials**, vol. 345, p. 128261, Aug. 2022. https://doi.org/10.1016/j.conbuildmat.2022.128261.

SANCHES, F. de O.; FIALHO, E. S.; QUINA, R. R. Evidências de Mudanças Climáticas em Viçosa (MG). **Geography Department University of Sao Paulo**, vol. 34, p. 122, 22 Dec. 2017. https://doi.org/10.11606/rdg.v34i0.138581.

SARASWATHY, V.; RENGASWAMY, N. S. Adhesion of an acrylic paint coating to a concrete substrate. **Journal of Adhesion Science and Technology**, vol. 12, no. 7, p. 681–694, Jan. 1998. https://doi.org/10.1163/156856198X00236.

SIAKENG, R.; JAWAID, M.; ASIM, M.; SIENGCHIN, S. Accelerated Weathering and Soil Burial Effect on Biodegradability, Colour and Textureof Coir/Pineapple Leaf Fibres/PLA Biocomposites. **Polymers**, vol. 12, no. 2, p. 458, 16 Feb. 2020. https://doi.org/10.3390/polym12020458.

SINGH, S.; NAGAR, R.; AGRAWAL, V. Performance of granite cutting waste concrete under adverse exposure conditions. **Journal of Cleaner Production**, vol. 127, p. 172–182, 2016. DOI 10.1016/j.jclepro.2016.04.034.

TRESSMANN, D. M. G. A.; PEDROTI, L. G.; CARVALHO, A. F. de; RIBEIRO, J. C. L.; CARDOSO, F. de P.; LOPES, M. M. S.; OLIVEIRA, A. F. de; FERREIRA, S. O. Research into the use of marble waste as mineral filler in soil pigment-based paints and as an active pigment in waterborne paints. **Construction and Building Materials**, vol. 241, p. 117976, 2020. DOI 10.1016/j.conbuildmat.2019.117976.

XIE, N.; LI, H.; ZHANG, H.; ZHANG, X.; JIA, M. Effects of accelerated weathering on the optical characteristics of reflective coatings for cool pavement. **Solar Energy Materials and Solar Cells**, vol. 215, p. 110698, Sep. 2020. https://doi.org/10.1016/j.solmat.2020.110698.

GENERAL CONCLUSIONS

1. FINAL CONSIDERATIONS

The present study investigated the potential utilization of granite and marble processing waste in cost-effective latex paints intended for civil construction. The mixture experiments allowed for the formulation of granite and marble waste paints with performance compatible with the requirements defined in technical standards, considering paints of the economic category. Among these two different types of residues, the granite waste provided better hiding power, abrasion resistance, and weathering resistance to the paints. This inert waste enabled the formulation of mixtures with high solid contents, leading to an enhancement in the optical properties of the paints while maintaining their viscosity within the range considered ideal for product application. Moreover, the high silica content of this waste possibly created a barrier against weathering, increasing the durability of the paints in outdoor environments. The smaller particle size also provided paint films with lower roughness, thereby enhancing abrasion resistance.

The addition of dispersant and biocide additives fulfilled their role in the paint formulations. The biocide additive significantly reduced bacterial growth in stored paint samples, without compromising their coverage properties and mechanical strength. The dispersant additive improved the particles dispersion and the hiding power of the paint film, but reduced its abrasion and weathering resistance. Therefore, it is important to exercise caution with the contents of this additive in the paint formulations.

Compared to natural weathering tests, accelerated weathering tests induced intense paint deterioration over a short period, allowing for a fast estimation of the behavior of paints in real conditions and predicting their lifespan. In this study, 16.6 days in the weathering chamber caused a level of deterioration similar to that observed after 12 months of natural exposure in a tropical climate Brazilian city. It is important to note that this relationship may vary for each exposure location.

In this context, it is concluded that the incorporation of marble waste and, especially, granite waste in paints is a new alternative for the utilization of ornamental stone processing residues in construction materials. This option allows for the reduction of impacts caused by inadequate disposal of these wastes in the environment and enables the manufacture of paints with good performance and low cost.

2. SUGGESTIONS FOR FUTURE WORKS

As suggestions for future work, the following areas could be explored:

- Utilization of other types of additives to enhance the performance and durability of paints produced with granite and marble waste.

- Testing paint formulations with different types of resins, such as acrylic resin, assessing the performance of new paints produced with granite and marble waste and facilitating comparison with commercial paints.

- Investigation into the influence of various types of waste grinding treatments (variations in grinding equipment, duration, speed, etc.) on the performance of sustainable paints.

- Cost-benefit evaluations of paints containing granite and marble waste should be conducted to assess the economic feasibility of the product.

- Testing the natural weathering of these paints in different regions over extended periods, and correlating these results with those obtained from the accelerated weathering tests.

- Determination of other paint properties, such as color and absorptance.