Please cite this article in press as: Mandal et al., Paints as a Scalable and Effective Radiative Cooling Technology for Buildings, Joule (2020), https://doi.org/10.1016/j.joule.2020.04.010

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Paints as a Scalable and Effective Radiative Cooling Technology for Buildings

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Introduction

As climate change and global energy consumption manifest in rising global temperatures and heat-islands, cooling living environments has become an urgent challenge. In developed settings, air conditioning of buildings consumes energy, generates heat, and releases greenhouse gases, exacerbating cooling needs. In regions of the world such as South Asia and sub-Saharan Africa, inadequate power infrastructure for cooling buildings has led to rising casualties during summers. Passive cooling technologies, which are sustainable alternatives or complements to active cooling methods, can address these issues. Here, we consider passive daytime radiative cooling of building envelopes and propose that white paints, which are well adapted for application on buildings and moderately good at radiative cooling, could be developed into highly efficient radiative coolers for buildings on a global scale.

Passive Daytime Radiative Cooling

Passive daytime radiative cooling (PDRC) involves the reflection of sunlight (wavelengths $\lambda \sim 0.3$–2.5 μm) and radiation of long-wave infrared (LWIR, $\lambda \sim 8$–13 μm) heat through the respective atmospheric transmission windows into outer space (Figure 1A). When a surface under the sky has a sufficiently high solar reflectance (R_{solar}) and LWIR emittance (ϵ_{LWIR}),[1] solar heating is outweighed by radiative heat loss to outer space, so the surface spontaneously cools, even under strong sunlight. The passive operation and net cooling effect overcome the disadvantages of active cooling methods. Since the surfaces of buildings exchange large amounts of heat with their environment as radiation, this makes PDRC attractive for cooling buildings.

Research on radiative cooling has a rich history, with materials like polymers (e.g., poly(4-methyl-1-pentene) and poly(vinyl fluoride)), dielectrics (e.g., SiO_X, ZnSe), polymer composites, and paints investigated for their cooling properties since the 1960s.[2,3] In the last decade, the field has seen a revival, with reported enhancements of earlier designs,[4–6] and new photonic[7] and polymeric[1] ones. While these are efficient at cooling, their utility depends on the application. For instance, photonic multilayer films, which can be tailored to have a high R_{solar} and selective ϵ_{LWIR}, attain deep sub-ambient temperatures useful for water-cooled HVAC systems, refrigerators, and thermoelectric devices.[7,8] While these emerging applications hold promise, cooling buildings remains the largest application of radiative cooling technologies. And although photonic designs have made strides in the area,[7] white "cool-roof" paints and materials, which have a modest R_{solar} ($\sim$0.8) and high ϵ_{LWIR} ($\sim$0.95), are currently the most widely used cooling approach for building envelopes. Given their inherent scalability, with enhancements in R_{solar}, paints thus have the potential to become an optimal solution for the radiative cooling of buildings.

Radiative Cooling Requirements

While reflective coatings on buildings are known to reduce solar heating, PDRC technologies go further to achieve heat loss even under sunlight, potentially doubling the cooling energy

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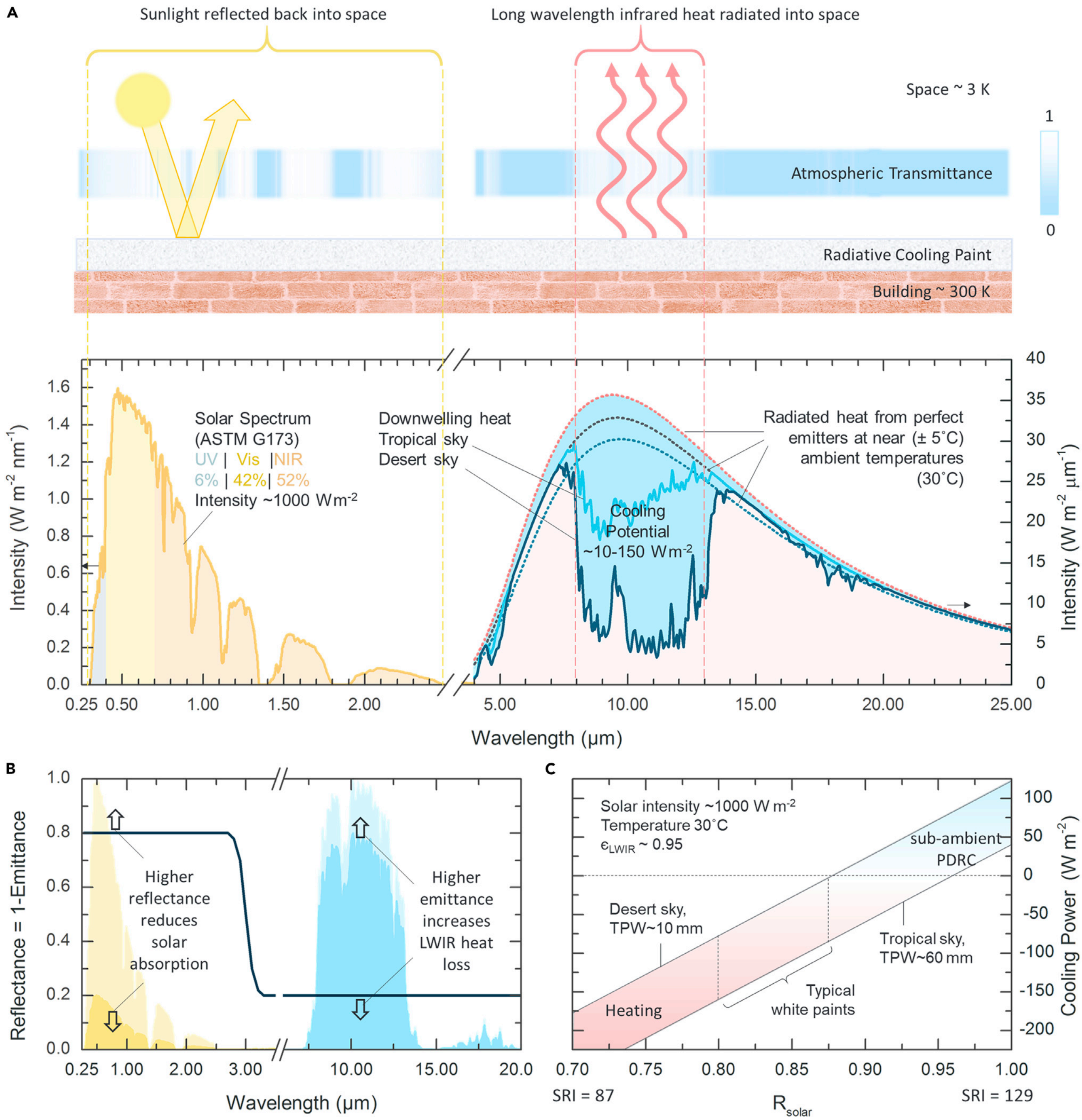

Figure 1. Radiative Cooling by a White Paint

(A) Schematic showing passive daytime radiative cooling by solar reflection and LWIR thermal emission through the atmospheric transmission windows. Corresponding solar and thermal spectra are shown below.

(B) Schematic showing how high solar reflectance and thermal emittance enable PDRC. It should be noted that at near-ambient temperatures, radiative transfer (= radiated heat from emitter – downwelling heat from sky) is small outside the LWIR window, making broadband and selective LWIR emitters similarly effective at cooling.

(C) Schematic showing cooling powers (= thermal emission – solar absorption)[1] of emissive coatings ($\epsilon_{LWIR} \sim 0.95$) as a function of R_{solar} (or solar reflectance index [SRI], which varies linearly with R_{solar}). $R_{solar} > 0.95$ usually yields sub-ambient radiative cooling.

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savings in buildings.[9] From a physical perspective, the requirements for PDRC building envelopes are well-defined (Figure 1B): (1) a high R_{solar} is required to minimize solar heating[1] and (2) a high ϵ_{LWIR} to maximize radiative heat loss to space.[1]

While the radiative cooling literature has emphasized the need for selective LWIR emittance to maximize cooling, it is only necessary for achieving optimal performance at temperatures substantially below the ambient.[2] Building envelopes on the other hand are typically at near- or above-ambient temperatures due to their contact with air and heat generation indoors. Hence, a broadband thermal emittance ϵ (across $\lambda \sim 2.5$–40 μm) subtending the LWIR wavelengths can be similarly effective at cooling as a selective LWIR emittance (Figures 1A and 1B). We note that with the development of robust, low-cost, and scalable IR-transparent insulation that prevents heating by air, selectively LWIR emissive materials could become more useful as building envelopes. However, at present, the suitability of broadband ϵ relaxes material constraints, as most non-metallic materials intrinsically exhibit high, broadband emissivity (Figure 2).

Practical requirements for radiative cooling building envelopes, however, impose further restrictions. For general global use, a PDRC building envelope should be (1) applicable on surfaces with various shapes, sizes, and textures, (2) resistant to ambient chemicals, solar irradiation, and the weather, and (3) affordable and accessible in different socioeconomic environments, particularly in the developing world.

A PDRC technology for building envelopes must therefore be sufficiently versatile, inexpensive, durable, and scalable, while still being effective at cooling. Having co-evolved with buildings, paints readily fulfil these practical requirements and currently present modest radiative cooling capabilities. Motivated by these observations, we investigate possible ways of enhancing the radiative cooling capabilities of paints and discuss broader issues related to their use as building envelopes.

Current PDRC Capabilities and Limitations of Paints

White cool-roof paints have long been established as a mature, scalable, and durable technology for cooling buildings, with studies showing that covering dark roofs ($R_{solar} \sim 0.3$) with such paints ($R_{solar} \sim 0.8$) can yield electricity savings of ~5 kWh m^{-2} $year^{-1}$ in hot climates.[10] However, a discussion of their potential as daytime radiative cooling surfaces remains missing in recent literature. Morphologically, paints are composites comprising optical scatterers, typically dielectric pigments, embedded in a polymer. A typical white paint contains TiO_2 pigments dispersed in acrylic or silicone in an ~1:1 mass ratio, with additional fillers like SiO_2 and $CaCO_3$.[4] These intrinsically emissive materials impart a near-unity, broadband ϵ of ~0.95 on paints. Indeed, the emissivity of typical paints are on par with, or even higher than, broadband emitters reported in the literature, making paints efficient at radiating heat into space.

The R_{solar} of paints, however, is lower than that of silver-based PDRC designs (~0.92–0.97) due to the industry's preferred use of rutile TiO_2 as the white pigment. TiO_2 nanoparticles' high refractive index ($n > 2.5$) relative to that of polymer binders ($n \sim 1.5$) enables them to scatter sunlight more effectively than the same amount of other white pigments, making TiO_2 cost effective. However, due to its bandgap of 3.0 eV ($\lambda \sim 0.413$ μm), TiO_2 intrinsically absorbs ultraviolet (UV, $\lambda \sim 0.3$–0.4 μm) and violet ($\lambda \sim 0.4$–0.41 μm) light, which carry ~7% of solar energy (Figure 2A). This restricts R_{solar} to <0.95 (Figure 2B). Research has led to the optimization of TiO_2 particle sizes to enhance scattering and approach that limit. However, near-infrared (NIR, $\lambda \sim 0.7$–2.5 μm) solar absorption by polymer binders (Figure 2A) and non-unity reflectance at other wavelengths mean that even with optimization, R_{solar} has a realistic limit of ~0.92 and is <0.86 for the best TiO_2-based paints (Figure 2B). These values meet current global "cool-coating" standards and keep coated roofs and walls significantly cooler than uncoated ones, but cannot yield sub-ambient cooling under strong sunlight (Figure 1C). Raising R_{solar}, however, can turn paints into radiative coolers that continuously lose heat to the sky regardless of the time of day, and therefore reduce cooling loads of buildings or bring relief during summers (Figure 1C).

Enhancing White Paints: Raising R_{solar}

While relatively rare in practice, the R_{solar} of white paints can be enhanced by material alterations. Since paints are optically inhomogeneous scattering media, removing any sources of absorption enhances R_{solar}. Two ways of doing so are (1) replacing TiO_2 with UV-nonabsorptive pigments and (2) using low-refractive index polymer binders with low UV and NIR absorptivity.

The first can be achieved in several ways. One possibility is to use pigments with wide optical band gaps, such as Al_2O_3 (7.0 eV, $\lambda \sim 0.177$ μm) and $BaSO_4$ (6.0 eV, $\lambda \sim 0.208$ μm). Another is using polymeric pigments like polytetrafluoroethene (PTFE) particles, which have minimal absorptance in the solar wavelengths. Notably, Al_2O_3, $BaSO_4$, and PTFE pigments have intrinsic optical phonon resonances or vibrational modes in the thermal infrared wavelengths, which make them suitable for radiating heat. A more novel, recently explored option is the use of microscopic air voids ($n \sim 1$) as "pigments" to scatter sunlight.[1]

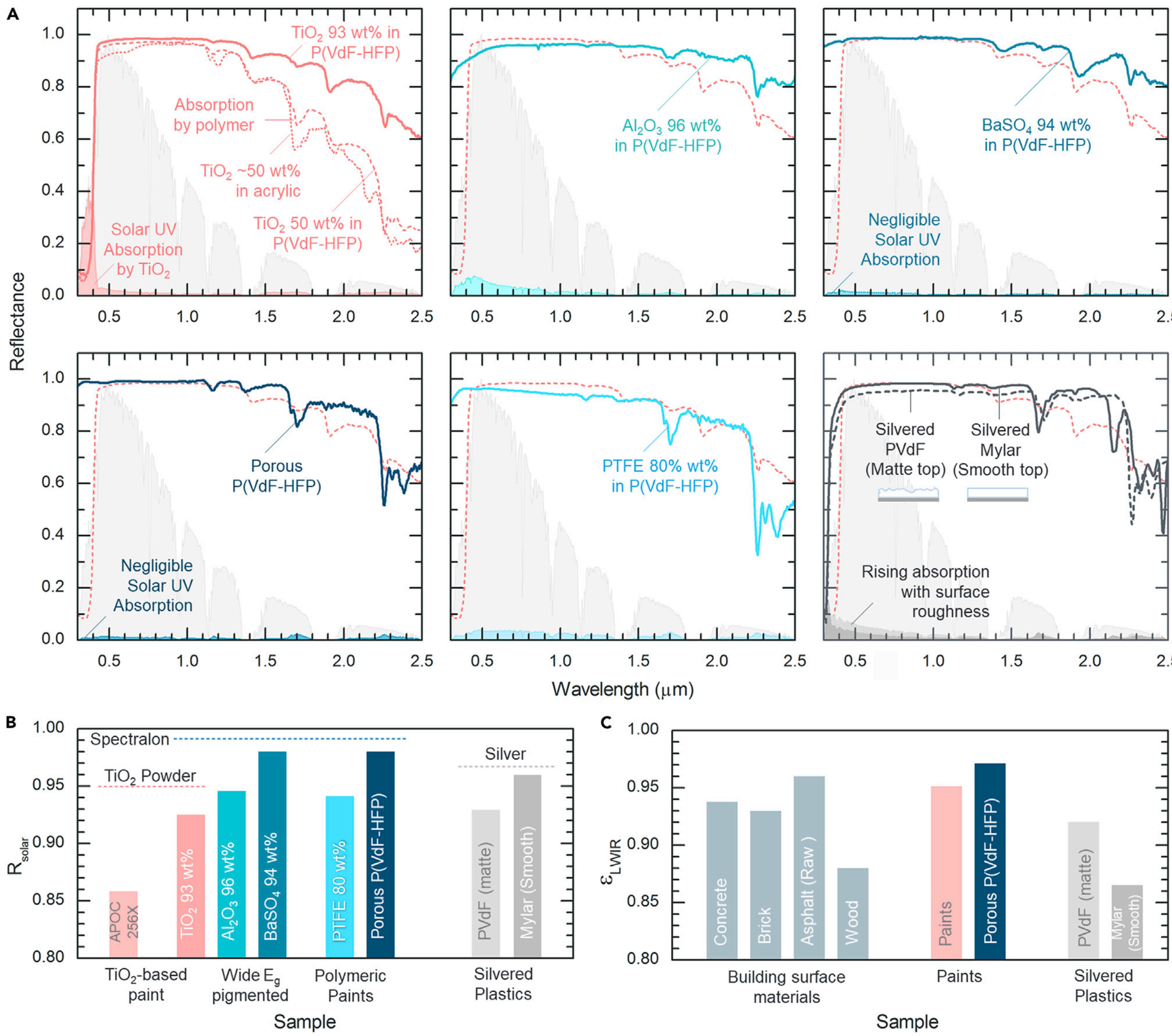

Figure 2. Optical Properties of Paints and Other Radiative Coolers

(A) Measured spectral reflectances of paints based on TiO2, Al_2O_3, $BaSO_4$, porous P(VdF-HFP) and PTFE, and silvered plastics (from top left to bottom right). The paint films are all ~1 mm thick.

(B) R_{solar} of paints and silvered plastics. APOC 256X paint is rated by the Cool Roof Rating Council as the most reflective on the market. The dotted lines show the reflectances of TiO_2 powder, spectralon (porous PTFE), and silver and represent the likely upper limits of R_{solar} of TiO_2-based, polymer-based, and silvered radiative coolers, respectively. Note that the reflectances were weighted using ASTM G-173 solar spectrum, which assumes a solar zenith angle of 48.19°. During summertime or in the tropics, the noon-time zenith angle is smaller. Consequently, UV light is stronger and further lowers R_{solar} of TiO_2 and silver-based designs.

(C) ϵ_{LWIR} of common building materials, paints, and silvered emitters.

In that case, the emittance ϵ arises solely from the porous polymer itself.

The second is achievable by using fluoropolymers such as P(VdF-HFP) or commercially available aqueous P(VdF) variants. Compared to acrylic or silicone, fluoropolymer variants have fewer C-H or O-H bonds, which absorb sunlight at $\lambda \sim 1.2$, 1.4, 1.7, and 2.3 μm, and more C-F bonds, which weakly absorb at ~2.1 μm. Moreover, fluoropolymers absorb less UV than acrylic, further enhancing R_{solar}. The absorptance can be further lowered by reducing the amount of polymer in the paint. Lastly, because fluoropolymers have lower refractive indices (~1.38–1.43) than acrylics (~1.495), they enhance scattering by pigments and, consequently, R_{solar}.

The above alterations are compatible with paint design and can significantly improve R_{solar}. Figures 2A and 2B show the results relative to reflectances of TiO_2-based white paints, a super-white PTFE-based reflectance standard (Spectralon SRM-99), and silvered emitters. Evidently, in the absence of intrinsic UV absorption, scattering by pigments results in high UV-blue reflectance. Reducing polymer content yields similar results in the NIR wavelengths. For the $BaSO_4$ and porous P(VdF-HFP) paint coatings, R_{solar} reaches ~0.98, and for the Al_2O_3 and the PTFE-based paint coatings, it exceeds 0.94. These reflectance values match or even exceed those of previously reported radiative coolers and, along with the high, broadband ϵ (Figure 2C), puts paints on par with state-of-the-art PDRC designs.

Complementing PDRC: Paints as a Mature Technology

The high PDRC potential of white paints is complemented by their generally low cost and ease of application on a broad range of surfaces. Furthermore, PDRC applications of paints can leverage advancements made by the coatings industry in chemical engineering for higher durability. Examples include coatings based on silicone, fluoropolymer, and cross-linkable binders that are resistant to UV damage and weathering and remain stable under the sky for years.

Due to their long-standing usage, paints also have a significant advantage of being a part of buildings-related energy policies worldwide. In the U.S., cities like New York and states like California have implemented policies favoring reflective coatings for buildings. Similar policies exist in global hotspots such as West and South Asia. Such policies may account for PDRC-capable paints as a natural extension of existing cool-roof standards and immediately expand their reach. Given these attributes and the optical performance achievable, paints emerge as a compelling and highly viable platform for the radiative cooling of buildings at large scales.

Challenges and Opportunities

While paints hold the potential to achieve optimal optical parameters for radiatively cooling building envelopes, challenges and questions remain. The major technical ones in our view are listed below, with potential solutions (Figure 3).

(1) Maximizing R_{solar} and ϵ_{LWIR} with minimal use of material. Cost remains a central challenge for any radiative cooling technology, including paints, where higher material costs could potentially be a roadblock. To mitigate this, and reduce material usage, we note that high ϵ_{LWIR} could be achieved by intrinsically emissive pigments with specific microscale sizes, or coating paints on emissive substrates. A high R_{solar} could be achieved by incorporating air voids ($n \sim 1$) in paints to increase optical scattering. Another possibility is bilayer designs that exploit the shallower penetration by shorter solar wavelengths in paint coatings (Figure 3). A thin layer of UV-reflective paint (Figure 2A) could be coated on a TiO_2 paint film, affording the high scattering efficiency of TiO_2 pigments while reflecting UV light from the top.

(2) Durability and resistance to soiling. Many conventional white paints, while engineered for durability, experience drops in solar reflectance over time. Materials such as fluoropolymer-based binders could enhance reflectance lifetime and thereby lower year-averaged costs. Soiling poses a challenge for all PDRC technologies as it reduces solar reflectance. Thus, designs that are resistant to soiling, such as hydrophobic, biofouling-resistant topcoats that can withstand physical cleaning, could maintain cooling performance and lengthen lifetime. Characterizing the weathering and failure modes of paints with such modifications will be essential for adoption by the construction industry.

(3) Reducing glare. While reflection off white paints is diffuse and less intense than those off silvered designs, it may harm eyesight and heat dark structures in view. Coating super-white paints with commercial high-index ($n \sim 1.9$) retroreflective spheres may address the issue. However, their impact on R_{solar} and ϵ_{LWIR} remains unexplored.

(4) Color as an aesthetic requirement and solution to glare. The industry has used selectively visible-absorptive colorants to create NIR-reflective paints. Recent innovations like fluorescent pigments that convert visible absorption to NIR emission,[11] and the bilayer design discussed above, where a selectively visible absorbing colorant is painted atop a broadband solar scattering layer, could be used to maximize the cooling performance while achieving color.

(5) In view of large-scale applications, reducing the environmental impact of paints. Currently, paints often use environmentally hazardous pigments that eventually "run off" into the environment or, for porous polymeric paints, may use toxic solvents like acetone.[1] Substitution of such materials with eco-friendly ones (e.g., water-based fluoropolymer variants), as well as enhancing the durability of paints to reduce their usage and release into the environment, would make paints more sustainable.

Additionally, we propose three broader challenges:

(1) Mapping the global geographical scope of radiative cooling paints, beyond which cold climates cause PDRC to increase annual

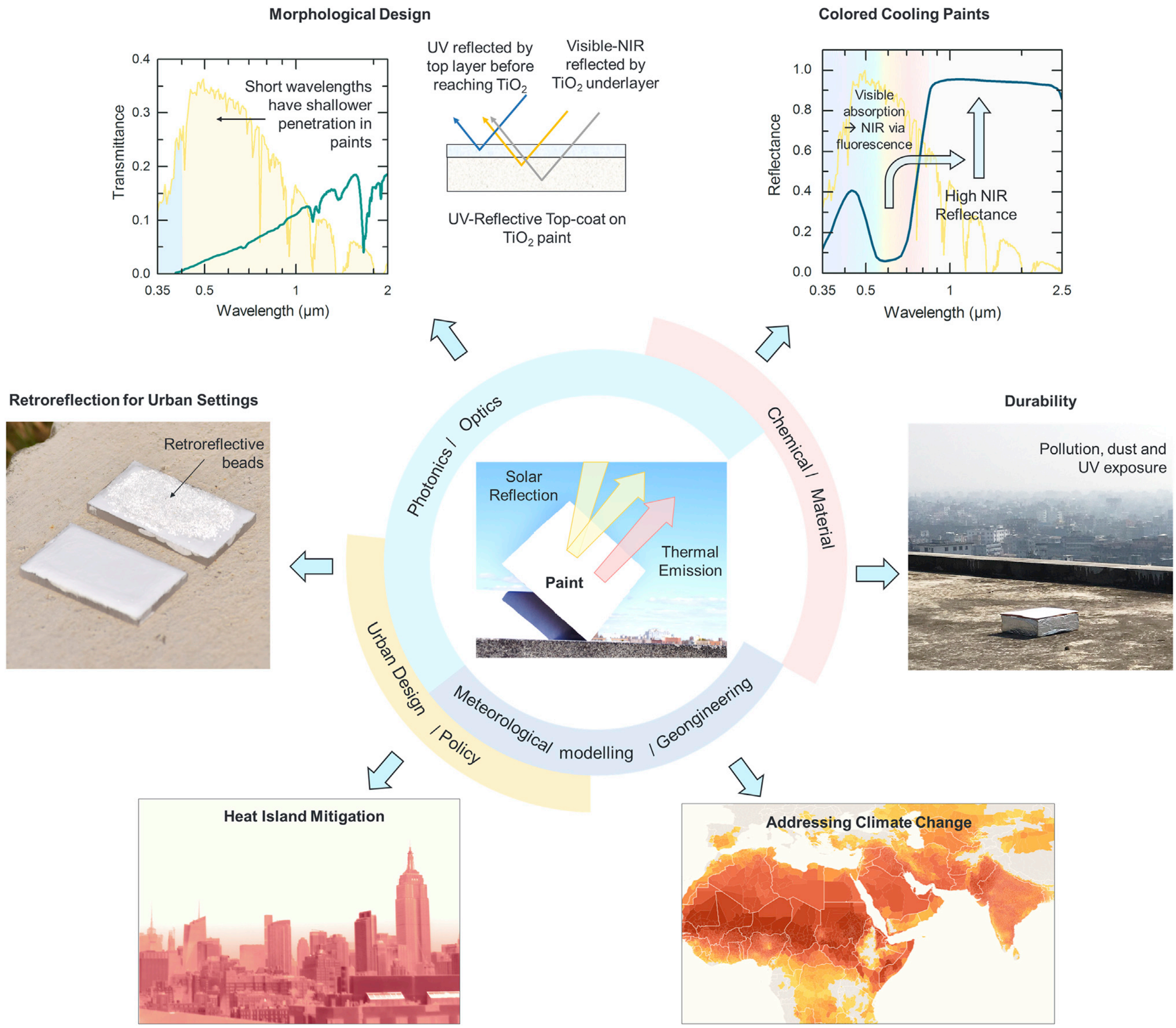

Figure 3. Some Issues Concerning Paints as a Radiative Cooling Technology for Use on a Global Scale
Addressing these issues requires collaboration across a wide range of disciplines, including optics, materials science, meteorology, and policy. The heatmap on the bottom right was obtained from the Climate Impact Lab website.

energy usage in buildings.[9] Among factors to be considered are clouds and anthropogenic particulates (see below), which can be transient and hinder both solar and LWIR transmission, as well as future variations of meteorological variables with climate change. This can aid resource allocation by private and public sectors in the field.

(2) Exploration of super-white paints as a "distributed geoengineering" tool,[12] where a fraction of roofs across the world are painted to raise the earth's albedo and reduce the climate impact of air conditioning by cooling the local environment,[9] while preventing weather disruptions that may arise from large-scale, centralized geoengineering. On a smaller scale, such an approach may also mitigate urban heat-island effects.

(3) Studying the effect of pollution and dust on the performance of radiative coolers. Many regions that stand to greatly benefit from radiative cooling technologies also see high airborne particulate and pollutant levels (e.g., South Asia; Figure 3). With the growing use of PDRC technologies, evaluating the relation between PDRC performance and pollution and dust (both airborne and settled on PDRC designs), and potential mitigation strategies (e.g., covering loose soil with vegetation, filtering

industrial emissions), can inform policymaking in those regions. Related studies for photovoltaic panels could be a useful guide in this regard.

Interdisciplinary Science to Address the Urgent Global Cooling Need

Holistically addressing the above challenges requires a convergence of expertise in fields like optics, materials science, and meteorology. Given the intensifying global need for cooling human environments and associated climate issues, an interdisciplinary approach to improve the already deployable solution in paints is perhaps the most practical way forward. While this piece highlights the exciting potential of paint coatings as passive daytime radiative coolers, we hope that it will spur further research that will establish super-white paints as a standard approach for radiative cooling of buildings worldwide.

ACKNOWLEDGMENTS

J.M. acknowledges support from Schmidt Science Fellows, in partnership with the Rhodes Trust, and thanks Professor Sir Keith Burnett for his valuable feedback on the work. A.P.R. acknowledges support from the Sloan Research Fellowship (Alfred P. Sloan Foundation).

DECLARATION OF INTERESTS

A patent (PCT/US2016/038190) has been granted, and a provisional patent (U.S. 62/596,145) filed related to prior works cited in the paper. A patent (U.S. 62/980,998) has been filed related to this work. A.P.R. is a founder of Sky-Cool Systems Inc., its chief scientific officer, and a member of its board. N.Y. is a founder of MetaRe.

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https://doi.org/10.1016/j.joule.2020.04.010