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Resistance of a Silicone Membrane to Long-term UV and Moisture Aging in Light of Climate Change

J-F. Masson¹, Peter Collins², Marzieh Riahinezhad^{3*}, Itzel Lopez-Carreón⁴, Jocelyn Johansen⁵

¹ Senior Research Officer, Construction Research Centre, National Research Council Canada, 1200 Montreal Road, Ottawa, ON, Canada K1A 0R6. Jean-Francois.Masson@nrc-cnrc.gc.ca

² Technical Officer, Construction Research Centre, National Research Council Canada, 1200 Montreal Road, Ottawa, ON, Canada K1A 0R6. Peter.Collins@nrc-cnrc.gc.ca

^{3*} Research Officer, Construction Research Centre, National Research Council Canada, 1200 Montreal Road, Ottawa, ON, Canada K1A 0R6. Marzieh.Riahinezhad@nrc-cnrc.gc.ca

⁴ Technical Officer, Construction Research Centre, National Research Council Canada, 1200 Montreal Road, Ottawa, ON, Canada K1A 0R6. Itzel.Lopez-Carreón@nrc-cnrc.gc.ca

⁵ Applied Research Chemist, CSL Silicones Inc., 144 Woodlawn Rd W, Guelph, ON, Canada N1H 1B5. JJohansen@cslsilicones.com

Corresponding author: Marzieh Riahinezhad (email: Marzieh.Riahinezhad@nrc-cnrc.gc.ca)

Abstract

Three room-temperature fluid-applied silicone membranes intended for application in the building envelope were studied in this work. The membranes were subjected to 5000 hours of accelerated UV and moisture aging to evaluate their resistance to long-term aging. The properties of the membranes were studied to understand any degradation mechanisms that might happen during accelerated aging. The weight loss, wetting propensity, cracking and oxidation resistance, and storage modulus were measured at different intervals during the 5000 hours of aging. Based on the material characterization results, the silicone membranes proved to be resilient under aggressive accelerated UV radiation and moisture aging, conditions which can be expected as a result of climate change.

Keywords: silicone, polymer, accelerated aging, membrane, barrier, microscopy, spectroscopy, modulus, water vapour permeance

1. Introduction

Buildings are most often designed for a minimum service life of 25 or 50 years (CSA Group 2019; Riahiinezhad et al. 2019). During this time, polymeric products on the buildings are exposed to intense and regular sunlight in normal applications. As a result, the average service life of these components is greatly reduced; for example, roofing membranes are generally in service for about 12 to 16 years (Cash 2003). Consequently, degraded components must be replaced several times during the life of a building, leading to challenges in waste disposal. Although recycling plans for construction and demolition waste are being developed and implemented around the world, certain aspects make the recycling of spent building construction materials challenging. For instance, separating contrasting materials that were well-fastened during the construction process can be expensive and time-consuming (Jeffrey 2011). In 2016, only 11% of plastic waste generated by the construction sector in Canada was diverted from going directly to the landfill (Solly et al. 2019). This is significant because the constructions sector generates a large amount of waste; it is the second largest market for plastic in the country and accounts for 26% of plastic put on the

market (Solly et al. 2019). Plastic and foam building and construction materials account for the majority of this fraction, therefore increasing the durability and service life of these products is important in reducing waste.

In addition to regular daily weather exposure, the advent of climate change, with higher average temperatures (Masson-Delmotte et al. 2018; Lacasse et al. 2020) and predictions of rising ultraviolet radiation (UV) levels from sunspot activity (Bhargawa and Singh 2019), may lead to an even shorter service life for standard building materials. Predictions also show that certain regions will receive more intense and frequent rain events, which would increase humidity levels in the atmosphere (Lacasse et al. 2020). Climate change is expected to continue in the near future, and projections show that global warming is likely to reach 1.5 °C above pre-industrial levels within the next decade or two if temperatures continue to increase at the current rate (IPCC 2018). In addition, warming rates are higher than the global average at high northern latitudes (Intergovernmental Panel on Climate Change 2013) such as northern Canada. **Figure 1** shows that between 1948 and 2016, the annual average temperature in Canada increased by 1.7 °C with respect to the reference period (1961-1990). During this same time period, the temperature on Earth as a whole increased by 0.8 °C (Zhang et al. 2019). Meanwhile, the annual average temperature in northern Canada increased by 2.3 °C, nearly three times the global average (Zhang et al. 2019).

Figure 1. Annual average temperature departures from the 1961 to 1990 reference value, Canada, 1948 to 2016 (blue), and linear trend (red). (Zhang et al. 2019)

Higher ambient temperatures and increased levels of UV are both known to accelerate the degradation of plastics and rubbers (Lacasse et al. 2020), and a combination of the two further expedites the process (Andrady et al. 2011). In the construction industry, plastics are increasingly replacing conventional materials due to their versatility and relatively low cost (Andrady et al. 2011). It is therefore important to study the weatherability and durability of new polymer-based building construction materials, under conditions that approximate what they will be experiencing during their service life, and through the lens of climate change. In this work, we report on the UV and moisture resistance of a silicone-based fluid-applied membrane intended for building envelope application. The technology of silicones takes its roots in the 1950's (Lewis 1962), but construction applications have been limited to a large extent to joint sealants (Amstock 2001); an application for which service life can exceed twenty years (Evans 2013). There is evidence that fluid-applied silicone membranes are used to protect blown in-place insulation in roofing applications (Cash 2003) and as roofing membrane applied onto concrete in tropical climates (Magnuson et al. 2015), but to our knowledge there is no work that reports on their resistance to weathering or

accelerated aging with both UV and moisture exposure. However, there have been studies looking at the UV degradation of silicones used in other applications, including outdoor high voltage insulation (Gorur et al. 1991; Yoshimura et al. 1999), encapsulating photovoltaic optical elements (Cai et al. 2016), and lenses in LED-based applications for outdoor environments (such as streetlamps) (Mehr et al. 2018). It is reported that the hydrophobic properties of silicone are retained upon UV aging of 6000 h (Gorur et al. 1991), and that short exposures (~ 700 h) lead to an increase in adhesion energy due to an increase in bonds between the silicone and the substrate, while longer exposures cause a subsequent decrease in adhesion energy due to embrittlement caused by photochemical crosslinking (Cai et al. 2016). The UV exposure conditions used in this study are more onerous than in standard testing, with an irradiance of 0.68 W/m^2 at 340 nm. This is twice the standard irradiance, which covers the potential rise in UV irradiance due to climate change. Results of surface and bulk properties indicate that silicone membranes, although not immune to aging, show very good UV and moisture resistance.

2. Experimental

2.1. Materials

Three proprietary room-temperature vulcanized (RTV) silicone roofing membranes were used in this work. RTV silicones cross-link (cure) with atmospheric moisture to form an elastomeric product upon curing (Lewis 1962; Moretto et al. 2012). All membranes were borne from a hydrocarbon solvent after they were sprayed onto a release surface. They were then cured for 10 days at room temperature and relative humidity, and then another 10 days at 60°C prior to UV aging. This was to ascertain that membranes would be fully cured before UV and moisture aging, which is also at 60°C . The three products differed in formulation based on their cure or application characteristics: Membrane A was formulated to cure in low temperature (winter blend); Membrane B was formulated to meet regulations for low emissions of volatile organic compounds (VOC); and Membrane C was formulated for standard summer applications. Additional details regarding the material properties of the three membranes are summarized in Table 1 below, where each value is the average of six replicate measurements.

Table 1. Silicone membrane properties.

	Product A	Product B	Product C
Grade	Winter	Low VOC	Summer
Thickness (mm)	0.62	0.41	0.51
Tensile Strength (MPa)	1.2	0.6	1.1
Elongation (%)	175	125	235
Modulus of Elasticity at 0 °C (MPa)	1.5	0.75	2.1

2.2. Accelerated aging

The silicone membranes were exposed to UV and moisture aging for 0, 500, 1000, 2000, 3000, 4000, and 5000 hours in a QSun Xe3-HDS accelerated aging weatherometer, equipped with Xenon lamps and Daylight-Q filters. The basis for the UV light exposure was standard method ASTM G155 with a UV irradiance of 0.68 W/m² at 340 nm. UV and moisture aging consisted in a repeating 12-hour cycle:

- a) 8h of UV irradiance and black panel temperature of $60 \pm 3^{\circ}\text{C}$.
- b) 4h of water-spray at a black panel temperature of $40 \pm 2^{\circ}\text{C}$

The membranes were exposed to 5000 hours of accelerated UV and moisture aging with a total of 3333 hours of UV lighting at an irradiance of 0.68 W/m² at 340 nm. This irradiance is the peak mid-day summer time irradiance in Toronto (Wypych 2008) and was maintained throughout the aging time. This is aggressive UV exposure in comparison with standard aging conditions. For instance, ASTM D6754/D6754M-15 (ASTM International 2015) on other polymeric roofing, calls for 4250 hours of UV light at 0.35 W/m², an irradiance closer to a daily average. These two conditions (this research study and the example from ASTM) provide for total irradiances of 2266 W.h/m² and 1487 W.h/m², respectively. Let us compare these conditions in more detail.

In 2017, the daily average global horizontal solar irradiance was 13.4 MJ/m² in Ottawa, and 13.7 MJ/m² in Toronto (Environment and Climate Change Canada 2020), two major cities in southern Canada. In the laboratory, each wavelength is taken as 1% of the total irradiance so that on an hourly basis, the higher

daily average solar irradiance converts to 2.365 MJ/m². Given that 1J = 1W.s, this further converts to 657 W.h/m². The UV aging conditions in this work thus represent an acceleration factor of 3.45 times over the natural exposure, and 1.5 times over that provided by standard conditions such as those in ASTM D6745/D6754M.

2.3. Analysis Methods

Membranes A, B, and C were characterized for both surface and bulk properties before and after accelerated UV and moisture aging. Characteristics included weight change, surface cracking, wetting resistance, oxidation levels, and storage modulus as detailed in the following sections. Analyses were done in duplicate. A 15 cm by 15 cm sample was used for weight change measurements, and a 10 cm by 15 cm sample was used for all other characterization methods. At each UV aging interval, a sample was cut and removed from the environmental chamber for analysis.

2.3.1. Weight change

Weight change was measured periodically on a balance (Sartorius, model E2000D) with a precision of 0.0001g, starting with a membrane close to 10 g in weight. Weight change is defined as follows:

$$\text{Weight change, \%} = ((\text{New weight})/(\text{Original weight}) \times 100) - 100$$

2.3.2. Optical microscopy

Surface morphology of the aged samples was studied by optical microscopy. Microphotographs were obtained on a Zeiss Stemi V11 microscope with a Clemex Captiva software. A magnification of 24X was used. Images were processed slightly for brightness and contrast in Microsoft Editor.

2.3.3. Wetting

Receding contact angles were measured by dynamic sessile drop method (Adamson 1990) with a Rame-Hart 200 contact angle goniometer controlled with the instrument software, Drop-Image. A drop of distilled water was placed onto the membrane surface with a micro-syringe. The volume of water was increased to the advancing contact angle limit and then reduced again past the receding limit. Contact angles were

measured during the receding portion of the test. The reported contact angle values are averages calculated from eight water drops.

2.3.4. Infrared spectroscopy

Oxidation levels were measured by infrared spectroscopy using a Thermo-Fisher Is50R Fourier-Transform Infrared Spectrometer with an attenuated total reflectance (ATR) accessory. The internal reflection element of the ATR was a single bounce diamond crystal set at an angle of incidence of 45°. Spectra were collected between 4000 – 400 cm^{-1} as the average of 32 scans at a resolution of 4 cm^{-1} .

2.3.5. Storage modulus

The storage modulus was measured on a TA Instruments Q800 dynamic mechanical analyzer in tension mode. Samples close to 20 mm by 6 mm x 0.5 mm were used for temperature sweeps between 22 °C and –145 °C at a cooling rate of 2 °C/min, a frequency of 1 Hz, an amplitude of 5 nm, and a loading force of 0.01N. Exact dimensions were measured prior to each run. The storage modulus (E'), loss modulus (E'') and tan delta ($\tan \delta$) were recorded, but we report here only on the storage modulus, which is similar to the common Young's modulus (E) (Nelson 1974).

2.3.6. Water vapour permeance

The water vapour permeance was determined in accordance with ASTM E 96-15, using the procedure for the Desiccant Method in section 11 of the standard. Samples were measured in triplicate at three levels of relative humidity: 26%, 36% and 45%. The average water vapour permeance is reported.

3. Results and Discussion

On aging silicone membrane formulations A, B and C up to 5000 hours, the material properties were studied on a regular basis and the results are presented in the following sections.

3.1. Weight Loss and surface morphology

The weight loss of each formulation, A, B and C is shown in **Figure 2**. All three membranes show a linear decrease in weight over aging time, with membranes A and C losing about 4 – 5% and membrane B losing about 7%. In an attempt to discern the reason for weight loss, the surface of the membranes were observed under a microscope to see if the surface erosion or other features were visible. However, there were no visible signs of surface change for any of the membranes during the aging periods: no cracking, crazing, or blistering. **Figure 3** shows the results for the unaged control and the membranes aged 5000 hours. In the unaged products, specks are visible here and there, possibly from fillers or pigments, or their small aggregations. On aging, however, these specks were somewhat more prevalent, which might indicate a very slight surface erosion, but on this basis, it would be difficult to substantiate the weight loss reported in **Figure 2**. The surface changes in **Figure 3** were not visible to the naked eye, which showed that the aesthetic aspects of the membranes were not changing upon accelerated aging.

Figure 2. Weight change in silicone membranes A, B, and C with aging time.

Figure 3. Surface morphology for Membrane A (left), Membrane B (middle) and Membrane C (right) by optical microscopy (5x) after 0 (top) and 5000h (bottom) of aging. The scale bar is the same in all photos, 300 µm.

3.2. Wetting

The wetting of water onto a surface is related to the surface polarity, and the wetting propensity is measured from the contact angle between a drop of water and the surface; the greater the angle, the more hydrophobic is the surface. Water shows an angle above 90° onto a non-wetting surface (Adamson 1990).

The water contact angle onto membranes A, B and C and their change on aging is shown in **Figure 4**. The initial contact angles were at 75° to 85° . These angles are far from 0° , so the unaged surface does not wet well. On aging, there was a 15° to 25° total increase in contact angle. It increased relatively rapidly in the first 1000 hours of aging (with membrane B having the greatest rate of change within the first 500 hours), followed by smaller increases for the rest of the aging regime. After 5000 hours of UV aging, the contact

angles rose above 90° , up to 100° . All membrane surfaces thus became slightly more hydrophobic with aging, a positive sign for a roofing membrane, whose function is to shed away water.

Figure 4. Wetting propensity of the membrane surfaces as measured by the receding contact angle of water.

3.3. Storage Modulus

The effect of UV and moisture aging on the storage modulus (E') of Membrane A is shown in **Figure 5**. All three membranes behaved similarly, so only the results for Membrane A are presented here. Likewise, the effect of aging time has fairly little effect on membrane rheology, and for improved clarity, the curves for 2000 h and 4000 h have been omitted in **Figure 5**. Starting with the control sample at 20°C , the modulus is low at 1.4 MPa. On cooling down to about -65°C , the modulus remains low, although it does rise to 3.3 MPa. This is the region of the rubbery plateau. Then on continued cooling from -65°C to -70°C , the modulus rises by three orders of magnitude to reach 1000 MPa due to the crystallisation of the silicone chains (Aranguren 1998; Bosq et al. 2014). At the rubbery plateau, the membrane is soft and elastomeric, whereas it is rigid below the crystallisation temperature. The trend is similar for aged samples at different aging intervals.

The evolution of the storage modulus at the rubbery plateau, measured at 0 °C, upon aging of the membranes is illustrated in **Figure 6**. The storage moduli of membranes A and C are close and follow a similar increase upon UV aging. In contrast, the storage modulus of Membrane B start lower, but it also increases with aging time, although at a slightly slower rate than membranes A and C.

The temperature at the onset of crystallization is shown in **Figure 7**. There is a 3 °C to 4 °C rise in the onset of crystallization upon aging. The onset for Membrane C reached a steady-state after 2000 hours of aging, whereas Membrane B reached a steady-state after 3000 hours. The rise in the onset of crystallization for Membrane A was not quite as regular as it increased from about –69 °C to –66 °C without reaching a steady-state. The results in Figures 5-7, indicate that silicone membranes would remain rubbery and elastomeric in normal winter conditions, even those encountered in the northern territories of Canada, where winter lows can reach –50 °C.

Figure 5. Temperature-dependent storage modulus and its variation with aging time in Membrane A.

Figure 6. Evolution of the storage modulus in the rubbery plateau at 0 °C upon UV aging of membranes A, B and C.

Figure 7. Evolution of the temperature at the onset of crystallization (T_c), where a rapid rise in modulus occurs on cooling.

3.4. Oxidation Resistance

The oxidation resistance of the silicone membranes was assessed by mid-infrared spectroscopy. **Figure 8** shows the spectrum for an unaged silicone membrane. The most intense absorbance of infrared light, labelled in **Figure 8**, arises from the Si-O-Si polymer backbone, Si-C bonds, and CH₃ side groups (Lin-Vien et al. 1991). On this basis, we can identify the membrane polymer as the most common silicone, namely, polydimethyl siloxane (PDMS) (Lewis 1962; Moretto et al. 2012), with its repeating unit being $[-(\text{CH}_3)_2\text{SiOSi}(\text{CH}_3)_2-]_n$.

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Figure 8. Mid-infrared spectrum for Membrane A. The source of the absorbance (peaks) is shown with labels.

The infrared spectra for Membranes A, B, and C, both before and after 1000, 3000 and 5000 hours of aging, are respectively shown in **Figures 9, 10, and 11**. The spectra at 500 hours, 2000 hours and 4000 hours were omitted to improve the clarity of the figures. On oxidation, new infrared absorbance (peaks) are generally

visible above 3000 cm^{-1} and between 1700 and 1800 cm^{-1} (Lin-Vien et al. 1991). In the current case, all three membranes showed very good oxidative stability on exposure to UV irradiance and moisture up to 5000 hours, as there was very little, if any, oxidation related bands in those regions after aging. Indeed, in the region around 3400 cm^{-1} , all membranes showed only a very slight increases in infrared absorbance from hydroxyl groups, -OH , whose intensity is never greater than a mere 0.01 Absorbance units in any of the membranes after any aging time. In a microscopic view of this small increase, it is seen that in Membrane A, the hydroxyl absorbance reached 0.01 Absorbance only after 5000 hours aging (**Figure 9, top**). In Membrane B, it occurred in two steps, with a first increase at 1000 hours, and then another at 5000 hours. In Membrane C, the intensity of this Si -OH band increased regularly from 0 to 5000 h. Based on these results, we can readily conclude that the oxidation resistance of the membranes were all very good, but not quite equal, with membrane A being the most resistant.

To determine a possible cause for the very slight oxidation, it is instructive to review the so-called fingerprint region of the infrared spectra for each membrane, that is, between 400 and 1900 cm^{-1} . Aging leads to variations in the peak at 1450 cm^{-1} , along with slight changes in the twin peaks at 1090 cm^{-1} and 1020 cm^{-1} . We attribute these peaks to the Si-CH_3 and Si-O-Si segments of PDMS, although there may also be other formulation compounds in the proprietary formulation with overlapping infrared peaks. This is especially true of the peak centered on 1450 cm^{-1} , which may arise from C-H signals from both the Si-CH_3 polymeric segment, and solvent traces. This peak decreases in intensity in parallel with the rise in hydroxyl group at 3400 cm^{-1} .

On the basis of the weight loss in **Figure 2**, the rise in contact angle in **Figure 4**, the slight rise in the rubbery modulus in **Figure 6**, and the changes in infrared spectra in **Figures 9 to 11**, we deduce that silicone membranes born from hydrocarbon solvent retain solvent traces upon spraying and curing, and that some Si-CH_3 are converted to Si-OH . These conclusions are supported by the following evidence obtained on UV and moisture aging:

- a) The membranes weight loss. PDMS has no vapour pressure at normal pressure, but hydrocarbons do, so once they accumulate at the surface where they change the water contact angle at the surface, from where they can evaporate during long-term UV aging at 60 °C.
- b) Contact angle rises. Hydrocarbons have low surface energies (Adamson 1990), and on aging, the hydrocarbon solvent traces migrate to the surface to lower the surface energy and increase the water contact angle.
- c) The infrared peak centered near 1450 cm⁻¹ goes down with aging. CH groups in hydrocarbons absorb at that wavelength (Lin-Vien et al. 1991). The decrease of this band on aging is consistent with a).
- d) The rubbery modulus rises on aging. Solvents can plasticize polymers to provide for softness (Billmeyer 1984). On aging, a loss of solvent as in a) provides for a more rigid polymer and a slight rise in modulus.
- e) Silanol groups, Si-OH, are formed. The reaction of two silanol groups, as per $2 \text{ Si-OH} = \text{Si-O-Si} + \text{H}_2\text{O}$, lead to some additional cross-links, which raise the modulus at the rubbery plateau (Ferry 1980). On the condensation of the two silanol groups, a water molecule is expelled, which is free to evaporate and contribute to weight loss.

Figure 9. Mid-infrared spectrum of Membrane A in the region of 3800 to 2600 cm^{-1} (top), and 1900 – 400 cm^{-1} (bottom). The spectrum of the control sample is in red, and those for the samples aged 1000, 3000, and 5000 hours are respectively in blue, green and gold.

Figure 10. Mid-infrared spectrum of Membrane B in the region of 3800 to 2600 cm^{-1} (top), and 1900 – 400 cm^{-1} (bottom). The spectrum of the control sample is in red, and those for the samples aged 1000, 3000, and 5000 hours are respectively in blue, green and gold.

Figure 11. Mid-infrared spectrum of Membrane C in the region of 3800 to 2600 cm^{-1} (top), and 1900 – 400 cm^{-1} (bottom). The spectrum of the control sample is in red, and those for the samples aged 1000, 3000, and 5000 hours are respectively in blue, green and gold.

3.5. Water vapour permeance

The effect of UV and moisture exposure on the water vapour permeance (WVP) of the three silicone roofing membranes is summarized in Table 2. After 5000 hours of weathering, Membrane B demonstrates the smallest change in WVP at the three levels of relative humidity tested, never deviating more than 4%. Membranes A and C both lose water vapour permeance, with Membrane A presenting the greatest loss, from 30% to 42% of its initial WVP. Nonetheless, all three formulations demonstrate high water vapour permeability before and after aging, giving the membranes a “breathable” quality that allows moisture to diffuse into and out of the roof assembly, preventing moisture from becoming trapped and condensing on the roofing components.

Table 2. Water vapour permeance data for unaged and aged (5000 h) membranes.

Formulation	Relative humidity, %	Water vapour permeance, ng/s.m ²		Change in WVP, %
		Unaged	Aged	
A	26	209.6	147.8	-29.5
	36	274.0	159.3	-41.8
	45	268.3	175.0	-34.8
B	26	177.1	171.2	-3.4
	36	181.1	186.7	3.1
	45	204.1	209.7	2.7
C	26	190.4	187.7	-1.4
	36	244.7	198.5	-18.9
	45	274.3	217.0	-20.9

4. Conclusions

In efforts to identify roofing products that may be superior in durability than common roofing materials, three formulations of a fluid-applied silicone membrane were evaluated for resistance to accelerated aging by exposing them to 5000 hours of water spray and ultraviolet light at an irradiance twice the standard levels. The products were evaluated for weight loss, wetting propensity, cracking and oxidation resistance, and change in rheological properties.

Although the UV aging conditions in this work represented an acceleration factor of 3.45 times over the natural exposure, and 1.5 times over that provided by standard conditions such as those in ASTM D6745/D6754M, the three silicone-based fluid-applied membranes intended for building envelope showed promising stability under the given test conditions. On aging, the three membranes proved practically equivalent; they showed no defects under the microscope, but they showed some weight loss – between 4%

and 7% – attributed to the escape of residual solvent. The silicones further resisted oxidation as they only showed extremely slight oxidation bands in analysis by infrared spectroscopy. In all cases, the membranes remained elastomeric on cooling down to at least $-60\text{ }^{\circ}\text{C}$, even after aging, and only displayed a slight increase in modulus of less than 1.0 MPa in the rubbery plateau region at $0\text{ }^{\circ}\text{C}$. Of the three membranes, formulation B retained its original water vapour permeance, while membranes A and C demonstrated a loss of WVP but nonetheless remained very permeable to water vapour after aging; all three membranes had a WVP of above 100 ng/s.m^2 at the three relative humidities tested. Based on these results, fluid-applied silicone membranes intended for building envelope applications would be expected to perform well in the widest range of service temperatures and UV exposures, including higher levels expected from climate change.

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