

# Interaction of N atoms through porous membranes in Nitrogen flowing post discharges

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## Abstract

This work reports on the results of investigations conducted with nonwoven membranes of different pore diameters: nylon (5  $\mu\text{m}$ ) and polypropylene (PP) exposed to a  $\text{N}_2$  flowing (1  $\text{L}_\text{n}.\text{min}^{-1}$ ) microwave (100 Watt) post discharge, produced at low gas pressure: from 130 to 4000Pa (1 to 30 Torr). The N atoms transmission through these membranes was measured from the intensity variation of the  $\text{N}_2$ , 580 nm afterglow which results of N atom recombination, before and after the membranes. It appeared that N-atoms penetrate and cross the membranes with a transmission factor varying from 20 to 50 % for nylon during the exposure time (less than 30 minutes). Such variations of the transmission factor are the result of the membrane etching by N-atoms. For the PP membrane, a nearly constant value of  $43\pm 3\%$  is found for the N-atom transmission without any remarkable etching effect. These results are discussed from the point of view of the membrane analysis (SEM, DSC).

## Introduction

Plasma modifications to change the surface properties of nonwovens for filtration processes such as gas separation, microfiltration, ultrafiltration, and pervaporation have been the subject of some publications [1–3].

In order to avoid any damage by plasma electrons and ion bombardment on the membranes, cold remote plasmas or post discharges are of interest as they allow interactions near the room temperature, in a large range of gas pressure to control the homogeneity of active species in a large volume of the reaction chamber. Microwave plasma post discharges of molecular gases are sources of active species for several surface treatments. In particular, previous studies have considered N atoms for iron surface nitriding [4], N and C atoms for iron nitrocarburizing [5], O atoms for elastomer activation [6] and for metal surface cleaning [7], and N and O atoms for bacteria inactivation [8] and for wool and polyamide 6 treatment [9, 10]. In each process, the densities of N, O, and C atoms can be determined by emission spectroscopy in the post-discharge reactor after calibration by NO titration [11].

Fundamental studies have been undertaken to determine the influence of N atoms on several surfaces. Measurements of the heat transferred to surfaces (metal, glass, and polymer surfaces), with deduction of the  $\gamma$  loss probabilities have been studied recently [12]. The treated surfaces have also been characterized by micrography and

X-ray diffraction for iron nitriding [4,5], by contact angle and XPS for the treatment of textiles [9,10] and by colony counting (CFU: colony forming unit) for bacteria inactivation [8].

Some correlations have been established between the density of active species (N and O atoms) and the effectiveness of surface treatment. However, in the surface reactions considering the respective roles of active atoms' penetration inside complex surfaces such as nonwovens, into interstices, holes, or tubes, of surface material etching and of surface heating, the question is still open. It is particularly important for bacteria or wool treatment.

In previous works the effect of pore diameter on N transmission through different membranes was evaluated [13, 14]. In the present work, we attempt to understand the influence of the fabrication method of a nonwoven, and its chemical and crystalline structure on its surface reactions by considering the transmission of the N atoms of an N<sub>2</sub> flowing microwave post discharge.

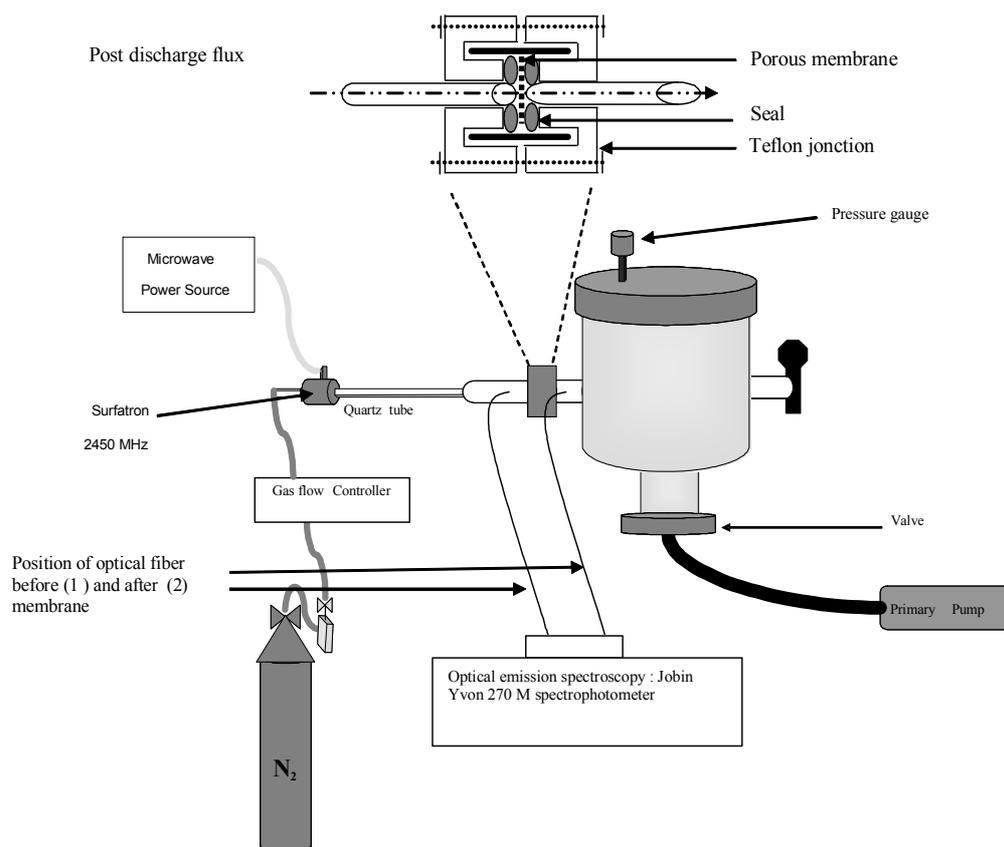
## **Experimental**

The transmission of N atoms was studied through nylon 6.6 and polypropylene membranes. The fabrication method of both membranes is different. Polypropylene membranes are nonwoven textiles prepared from polypropylene fibres by a melt-blown process, while nylon 6.6 membranes are prepared from a nylon solution extruded film which is then submerged into a co-solvent bath. This co-solvent is immiscible with nylon, producing coagulation of the nylon and pore formation during heat drying of the film.

The flowing discharge and post-discharge reactor is reproduced in Fig.1. The microwave discharge is sustained in a quartz tube of 5 mm internal diameter (i.d.) by 2.45 Ghz continuous surface waves, excited by a surfatron cavity. The discharge tube is sealed to a tube of 18 mm i.d. which is connected to a 5 litre Pyrex reactor (15 cm i.d. and 20 cm height).

The N<sub>2</sub> gas was introduced with a flow rate of 1 L<sub>n</sub>.min<sup>-1</sup> and the pressure in the post-discharge chamber was adjusted between 200 Pa (2 mbar, 1.5 Torr) and 5300 Pa (53 mbar, 40 Torr) by means of a throttle valve. The microwave (MW) continuous power was fixed to 100 Watt. The plasma and afterglow emission were collected by a quartz optical fibre (which can be fixed in position 1 or 2 – before or after the membrane) and sent to the entrance slit of a Jobin-Yvon 270 M (focal length of 27 cm) spectrometer, equipped with a CCD detector.

In order to study the transmission of N-atoms through the nonwovens, the membranes were set-up across the 18 mm i.d tube as detailed in Fig.1, in the afterglow after the 5 mm i.d discharge tube and before the reactor inlet.



*Fig. 1. MW flowing afterglow reactor. Detail of the membrane insertion in a Teflon junction in the 18mm id quartz tube.*

The crystallinity of the membranes was studied by differential scanning calorimetry. Crystallinity was calculated from the determination of the melt enthalpy with a differential scanning calorimeter (Mettler Toledo DSC826). The crystallinity is the ratio between the measured melt enthalpy and the melt enthalpy of a 100% crystalline polymer, which is of  $205 \text{ J g}^{-1}$  for nylon 6.6, and of  $207.1 \text{ J g}^{-1}$  for polypropylene [15].

## Results and discussion

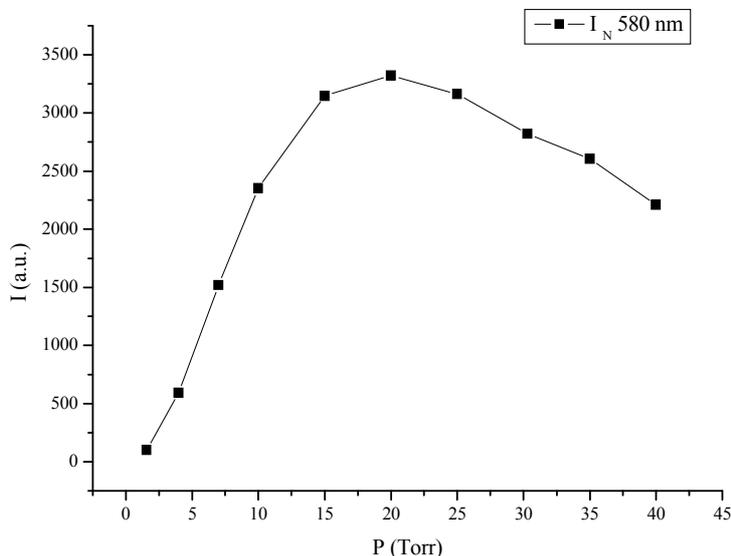
### Transmission of N-atoms through porous membranes

In the first place, the effect of upstream gas pressure on the production of N atoms (fig. 2) was studied in position 1 (see fig. 1). In a pure  $\text{N}_2$  late afterglow, the first positive emission intensity at 580 nm, coming from the  $\text{N}_2$  (B,11) which is populated by recombination of two N-atoms and thus proportional to  $[\text{N}]^2$ , according to equation 1 [16]:

$$I_{\text{N}_2} = C_1 [\text{N}]^2 k_1/k_2 \quad (1)$$

Where  $k_1$  and  $k_2$  are the recombination and quenching rates of the  $\text{N}_2$  (B,11) state, respectively.

As observed in fig. 2, by closing more and more the throttle valve, an increase of the  $I(N_2, 580 \text{ nm})$  intensity is observed (Fig. 2) when increasing the pressure from 2 Torr until a maximum reached around 20 Torr. With higher pressures the emission intensity decreases, which can be explained by a decrease of electron temperature and thus of  $N_2$  dissociation by electron collisions.



*Fig. 2. Variation of  $I(N_2, 580 \text{ nm})$  intensity with  $N_2$  gas pressure ( $N_2$  flow rate  $1 \text{ Ln min}^{-1}$ , microwave power 100 Watt) without membrane, obtained by closing the throttle valve (position 1).*

Transmission of N-atoms through nylon, PDVF and polysulfone porous membranes has been previously reported [1,2] and discussed in terms of the different porosity of the membranes. The transmission of N-atoms through a polypropylene (PP) membrane is reported here. The porous membrane was setup inside the Teflon junction as detailed in Fig.1.

The  $N_2$  1<sup>st</sup> positive emission spectra is shown in positions 1 and 2 (before and after the PP nonwoven membrane, respectively) in Fig. 3, at different treatment times.

A weak decrease of intensity in position 1 from 1200 to 900 cc is observed in Fig.3a. According to Fig. 2, it can be the result of a weak decrease of the  $N_2$  upstream pressure from about 7 to 5 Torr.

Figure 3 shows that the  $I(N_2, 580 \text{ nm})$  intensity, coming from the  $N_2$  (B,11) state, is the most intense band, characterizing a pure  $N_2$  late afterglow [16]. Consequently, equation 1 can be applied, the intensity  $I(N_2, 580 \text{ nm})$  being proportional to the  $[N]^2$  allows to determine the N-atom transmission ( $T_N$ ) through the PP membrane. From the results in Fig. 3 b, a  $T_N = 0.43 \pm 0.03$  is obtained.

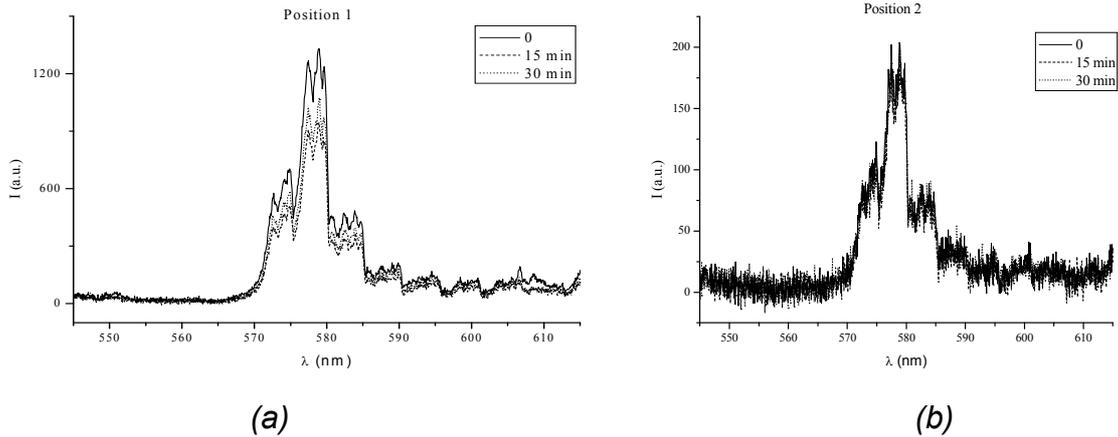


Fig. 3 Vibrational distribution of  $N_2(B, v')$  states of the sequence  $\Delta v = 4$  (resolution 1 nm) in (a) position 1 (upstream the PP membrane) and (b) in position 2, downstream. The maximum intensity is for the  $N_2(B, v'=11 - A, v''=7)$  band at 580 nm. Discharge conditions:  $N_2$ ,  $1 \text{ L}_n\text{m}^{-1}$ , 4 Torr downstream in the 5 litre reactor, 100 Watt in the microwave plasma.

Fig. 3b reveals nearly unchanged intensity behind the PP membrane with treatment time. Therefore,  $T_N$  is nearly constant for afterglow times up to 30 minutes. This contrasts with the results obtained with the nylon 6.6 membrane (fig. 4) [13], in which there is a significant intensity increase with treatment time, corresponding to an increase of  $T_N$  (nylon  $5 \mu\text{m}$ ) from 0.2 to 0.5 after 30 minutes of afterglow time. As reproduced in Fig. 5,  $N_2$  post-discharge treatment increases the membrane pore size through etching reactions of N atoms with the nylon surface.

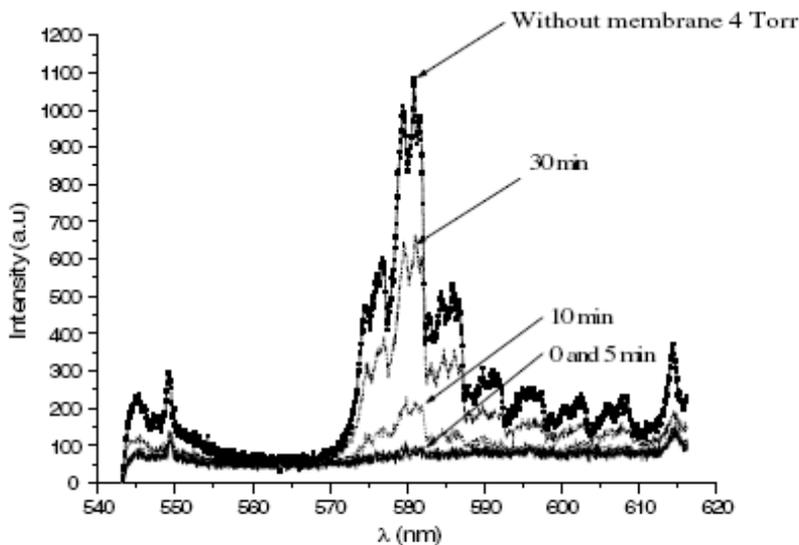
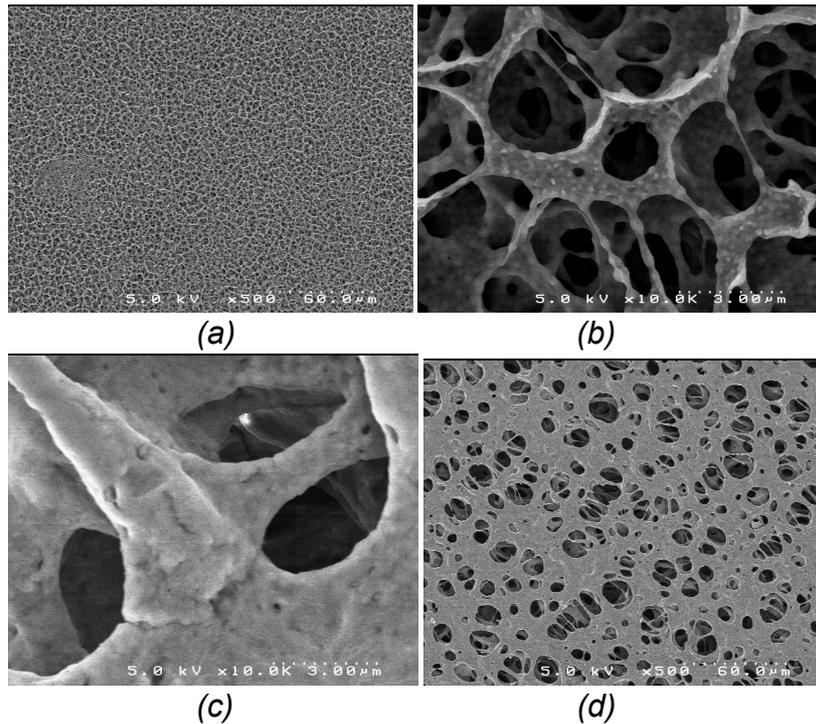


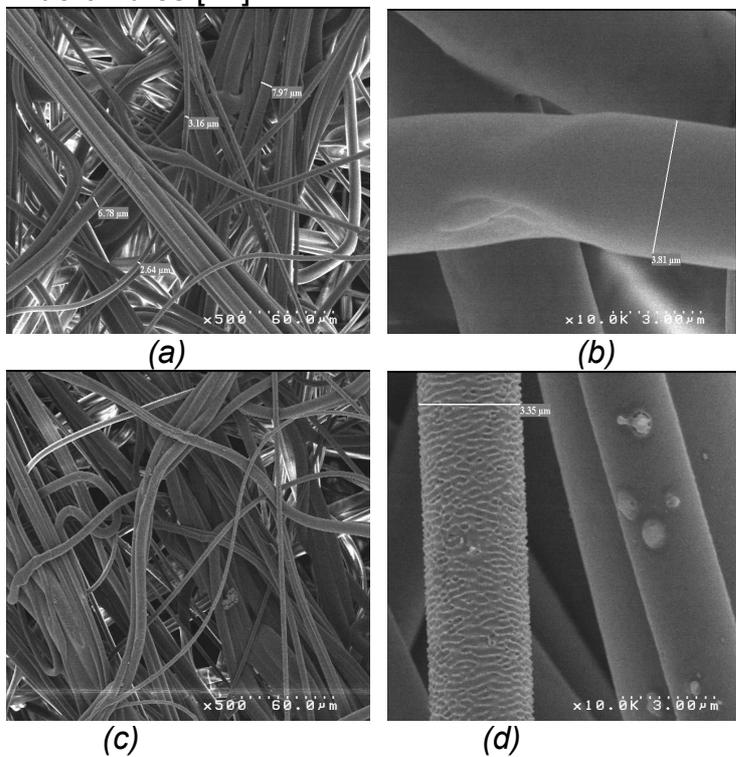
Fig. 4. Emission spectra of the  $N_2$  first positive emission in position 2, downstream the nylon 6.6 membrane. Discharge conditions:  $N_2$ ,  $1 \text{ L}_n\text{m}^{-1}$ , 4 Torr downstream in the 5 litre reactor, 100 Watt in the microwave plasma [1] (with permission of the editor).

Investigations with other membranes also found  $T_N$  transmissions increase after 30 min afterglow, from 0.5 to 1 with PDVF (pores  $1 \mu\text{m}$ ) and from 0.33 to 1 with polysulfones (pores  $1\text{-}3 \mu\text{m}$ ) [14].



**Fig. 5.** Scanning electron micrographs of nylon 6.6 membranes (a) and (b) untreated and (c) and (d)  $N_2$  plasma treated for 5 min [13].

In the case of the PP nonwoven membrane, the constant  $T_N$  factor found is consistent with the SEM micrographs, which do not show any pore size change or significant global etching effects (Fig. 6). Only some isolated PP fibres reveal some surface etching (fig. 6d), perpendicular to the fibre axis, as observed for plasma treated polyamide 6 fibres [17].



**Fig. 6.** Scanning electron micrographs of polypropylene membranes (a) and (b) untreated and (c) and (d)  $N_2$  plasma treated for 5 min.

Previous results on the treatment of polymer fibres with plasmas pointed out to preferential etching effect on low crystallinity regions (amorphous regions) [17]. It is known that the drawing of the fibres during the spinning process to produce fibres produces orientation of the polymer chains in the fibre axis resulting in increased crystallinity. According to the fabrication process of the nylon and polypropylene nonwovens, as well as to the SEM micrographs, it can be speculated that the melt-blown spinning process of PP produces a polymer with higher crystallinity than the nylon obtained from a non-oriented polymer film, which is more easily etched by N atoms.

This is confirmed by the Differential Scanning Calorimetry analysis shown in fig. 7, which gives a crystalline fraction of 36% for nylon 6.6, and, as expected, a slightly higher 42% for polypropylene.

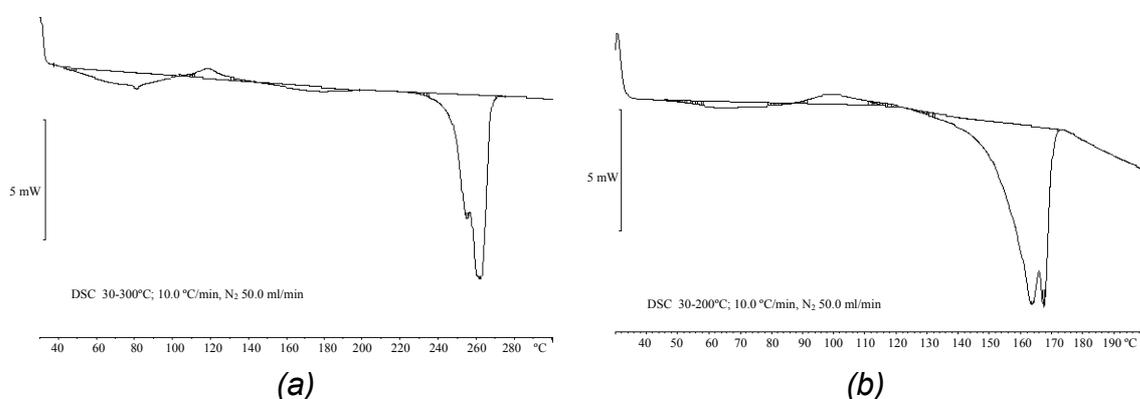


Fig. 7. Differential Scanning Calorimetry spectra of the untreated (a) nylon 6.6 and (b) polypropylene nonwoven membranes

In addition to that, the chemical structures of both polymers have to be taken into account in what regards the etching effect (see Fig. 8). The presence of amide bonds in the nylon molecule provides a point with higher reactivity towards the N atoms than the aliphatic C-C bindings present in the PP molecule, justifying the intense etching effect observed in nylon membranes.

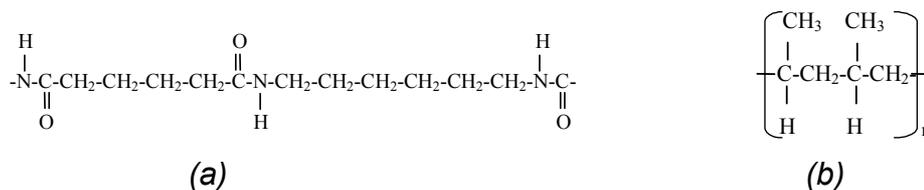


Fig. 8. Chemical structure of the nylon 6.6 (a) and (b) polypropylene membranes

### Concluding remarks

Transmission of N-atoms through polypropylene membranes was determined in a pure N<sub>2</sub> afterglow. A transmission factor (T<sub>N</sub>) of 0.43 ± 0.03 was found, without marked variations over 30 minutes of N<sub>2</sub> afterglow. This result indicates a weak etching of the polypropylene membrane by N- atoms, contrary to nylon 6.6 or other PVDF and polysulfone membranes previously studied. The differences in T<sub>N</sub> and topographical changes observed for nylon and polypropylene, attributed to the

etching effects observed, were explained by the greater percentage of amorphous regions in nylon 6.6 than in polypropylene, as well as the presence of the reactive amide bond in the chemical molecule of nylon, which makes it more prone to react with N atoms.

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