https://alertdiver.eu/de_DE/artikel/unsichtbare-kristalle-und-atemreglerausfaelle

15 Feb 2018 | François Burman

Unsichtbare Kristalle und Atemreglerausfälle

Ausfälle oder Fehlfunktionen bei Tauchausrüstungen sind relativ seltene Ursache von Tauchunfällen mit und ohne Todesfolge. Wenn es soweit kommt, handelt es sich meist um gefährliche Fehlfunktionen von Atemreglern oder den Inflatoren an Tarierwesten.[1]Daher war die Nachricht, die DAN vor Kurzem zu einer Reglerfehlfunktion erhielt, keine wirkliche Überraschung. Die Ursache dafür stellte sich aber als äußerst ungewöhnlich heraus.

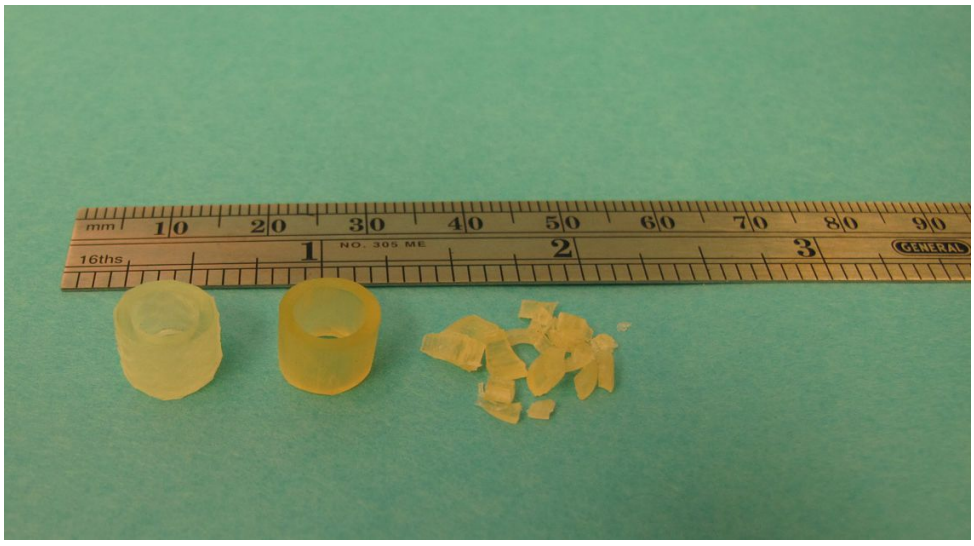
Obwohl die in den Vorfall verwickelten Taucher die Situation sehr gut im Griff hatten und niemand zu Schaden kam, hätte ein unerfahrener oder nervöser Taucher vielleicht nicht so viel Glück gehabt. Besonders bemerkenswert war, dass die Flasche des Tauchers nicht leer war, das Atemgas aber immer langsamer ausströmte und schließlich wie in einer Out-of-air Situation ganz versiegte. Die genauere Untersuchung der Ausrüstung führte zu einer rätselhaften Entdeckung: eine große Menge an gelbem „kristallisiertem“ Material verstopfte die Innenseite des Einlaßventils der zweiten Stufe. Das Material schien aus dem Inneren des Schlauchs zu kommen, der zwar schon ein paar Jahre in Gebrauch war, aber äußerlich keine Unregelmäßigkeiten oder Abnutzungserscheinungen zeigte.

Beim Versuch, das Rätsel zu lösen, entdeckten wir, dass es sich hierbei um keinen Einzelfall handelte. Die gleiche Situation war schon in einem Tekk-Taucher-Blog[2]beschrieben worden und auch von Schlauchherstellern und Wartungswerkstätten in beliebten Tauchgebieten. Obwohl bislang keine Verletzungen gemeldet worden waren, führte die Entdeckung dazu, dass das Ganze auf einer breiteren und globalen Ebene untersucht wurde.

Auf Nachfrage erhielten wir von einem großen Schlauchhersteller einen interessanten Rat: Schläuche halten nicht ein Leben lang und insbesondere Gewebeschläuche sollten alle fünf Jahre ersetzt werden - oder sogar öfter, wenn sie eindeutige Anzeichen von Verschleiß zeigen oder lange Zeit tropischer Sonneneinstrahlung ausgesetzt sind. Hinzu kommt, dass einige Schläuche, die unter den Markennamen seriöser Schlauchhersteller verkauft werden, in Wirklichkeit Imitationen sind.

Ein begeisterter Taucher, Ingenieur bei einem privaten Unternehmen in den USA, bot an, Niederdruck-Gewebeschläuche einer gründlichen Prüfung zu unterziehen. Er ließ verschiedene Schläuche auf künstlichem Weg schneller altern und fand zunächst einmal heraus, dass Schläuche mit einem Innenmaterial aus thermoplastischem *Polyester*-Polyurethan (Polyester-TPU) während der Untersuchung zerfielen. Dieses Ergebnis entspricht auch den Berichten, die DAN zum Thema Schlauchversagen gesammelt hat. Andererseits versagten Schläuche, die aus thermoplastischem *Polyether*-Polyurethan (Polyether-TPU) bestanden oder deren Innenseite damit beschichtet war, nicht.

Ein bekannter europäischer Hersteller von Gewebeschläuchen, der seit jeher Polyether-TPU verwendet, verlangt von seinen Materialzulieferern seit 2008, dass diese die Polyether-TPU-Innenbeschichtung bescheinigen.



Wie kommt es zum Zerfall der Innenbeschichtung?

Das Zerfallsprodukt, eine gelbe kristallähnliche Substanz, ist weicher als es scheint und fühlt sich an wie Wachs, wenn man es zusammendrückt. Die Reaktion, die den Zerfall verursacht, ist eigentlich Hydrolyse und für diese ist, wie der Name schon sagt, Wasser erforderlich. Eine erhöhte Temperatur fördert den beschleunigten Abbau bzw. die Hydrolyse von Polyester-TPU. Wiederholtes zyklisches Erhitzen und Abkühlen der Innenbeschichtung des Schlauchs fördert diese Form der Kristallisation bei Materialien, die entweder für eine solche Verwendung ungeeignet sind oder durch bestimmte Chemikalien oder Bakterien beeinträchtigt werden. Die Sonne heizt den Schlauch auf und dann kühlt das Atemgas die Innenseite des Schlauchs wieder ab. Dieser Prozess wiederholt sich bei jedem Tauchgang und die „Kristalle“ sammeln sich im Laufe der Zeit an. Es bilden sich schließlich genügend „Kristalle“, die den Gasfluß behindern bzw. die in Richtung des Reglers der Zweiten Stufe wandern. Das führt letztendlich zu einem schwerwiegenden Ausfall des Atemgeräts.

Es ist schwer vorherzusagen, wie lange der Zerfall einer Innenbeschichtung aus Polyester-TPU dauert, aber die uns vorliegenden Informationen lassen vermuten, dass dies bei freiliegenden Schläuchen bei 30°C und hoher Luftfeuchtigkeit in relativ kurzer Zeit der Fall sein kann.

Ausrüstungshersteller wurden über dieses Phänomen informiert und haben daraufhin ihre bestehenden Lieferanten sorgfältig überprüft und verbesserte Maßnahmen zur Überprüfung des Materials und zur Qualitätssicherung umgesetzt.

Die Standard-Sicherheitsempfehlung für Reglerschläuche lautet, dass diese regelmäßig auf Anzeichen externen Verschleißes hin untersucht werden sollten. Wenn die äußere Gummischicht zerfällt oder verschleißt, werden die Schläuche letztendlich anfällig und können reißen, wenn sie unter Druck stehen bzw. im Einsatz sind. Tatsächlich sind Gummischläuche hierfür recht anfällig, weshalb Polymer-Gewebeschläuche entwickelt wurden. Aber hier liegt das Problem: Bei einer flüchtigen Kontrolle der äußeren Oberfläche kann die Außenseite der Gewebeschläuche normal, beweglich und fehlerfrei erscheinen, während der Zerfall im Inneren unentdeckt bleibt.

Was empfiehlt DAN?

Es ist uns wichtig, Tauchern Folgendes zu raten:

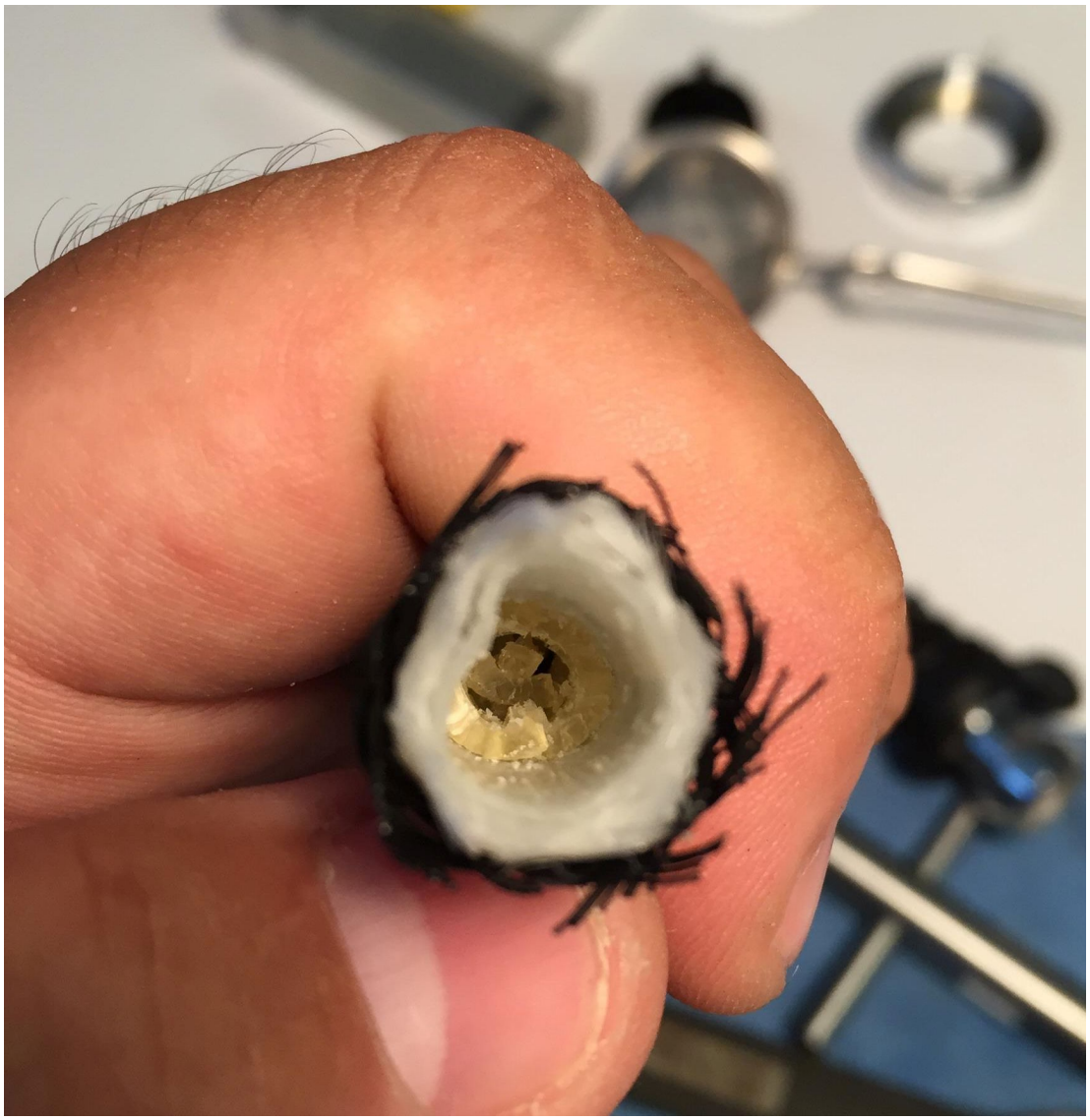
• Alle Reglerschläuche, auch Gewebeschläuche, haben eine begrenzte Lebensdauer, und zwar ganz unabhängig von ihrem äußeren Erscheinungsbild, einer Verstärkung bzw. einem Schlauchschutz oder dem Gewebe selbst. Die defekten Schläuche, die wir gesehen haben, waren mehr als fünf Jahre alt.

• Beim Kauf eines Schlauchs sollte man die Zusammensetzung der Innenbeschichtung prüfen - sie sollte aus Polyether-TPU und nicht aus Polyester-TPU bestehen. Falls man

sich nicht sicher ist, sollte man den Schlauch nicht kaufen. Man sollte sein Schläuche und andere Ausrüstungsteile, die der Sicherheit dienen, von namhaften Herstellern beziehen, die eindeutig deklarieren, welches Material für die Innenbeschichtung verwendet wurde.

• Wenn es irgendwelche Anzeichen dafür gibt, dass die Gaszufuhr eingeschränkt ist, sollte der Taucher den Atemregler sofort nicht mehr verwenden. Das gilt vor allem für neuere Schläuche. Der Regler und der Schlauch müssen dann sorgfältig geprüft werden. Wenn der Regler nicht die Ursache ist, liegt es vermutlich am Schlauch.

• Man untersucht Schläuche, indem man sie Zentimeter für Zentimeter zusammendrückt, um festzustellen, ob sie gleichmäßig beweglich sind. Jede Änderung dieses Widerstands, die auftritt, während man den Schlauch der Länge nach zusammendrückt, deutet auf ein mögliches Problem hin. Dieser Test lässt sich mit Gewebeschläuchen viel leichter durchführen als mit Gummischläuchen.



Wir bitten alle Taucher, die einen solchen Verschleiß bei der Schlauchinnenbeschichtung beobachten, unter **communications@daneurope.org** eine E-Mail an DAN zu senden - am besten mit Bildern, die den Zustand des Schlauchs demonstrieren. So können wir so viele Informationen wie möglich sammeln und mehr über dieses Phänomen lernen. Erkenntnisse, Sicherheitshinweise und Ratschläge werden wir natürlich an die Taucher-Community weiterleiten.

Referenzen

1. Vann R, Lang M. Recreational diving fatalities. Undersea Hyperb Med 2011; 38(4): 257-60.

2. Davis A. **Nylon-braided regulator hose diving emergency**. Scuba Tech Philippines. 22. Juli 2015. Geprüft 7. Dezember 2016.

http://scubatechphilippines.com/scuba_blog/regulator-hose-diving-emergency/#Polymorphic_Crystallization

http://www.danap.org/DAN_diving_safety/polymorphic_crystallisation.php

POLYMORPHIC CRYSTALLISATION' IN 'NYLON-BRAIDED' HOSES

AN IMPORTANT BUT 'INVISIBLE' CAUSE OF SECOND-STAGE SCUBA REGULATOR FAILURES

Francois Burman Pr. Eng. MSc

Continued from Deeper with DAN, July 2016

Generally speaking, SCUBA equipment failure or malfunction is a relatively minor cause of diving-related accidents and fatalities. It does occur, of course, with BC power inflator and regulator malfunctions being the most common and hazardous(1). As such, it was not unusual for a case of SCUBA regulator failure to be reported to DAN earlier this month. The cause, however, turned to be quite an unusual one…

Although the diver involved in the incident managed the situation very well, and no-one was harmed, other divers - especially inexperienced or nervous divers - might not have been so fortunate. What was particularly strange was that diver's cylinder was not empty. Yet, the flow of gas had slowed and then ceased in a way not unlike an out-of-air situation. Closer examination of the equipment led to another puzzling discovery: a large amount of yellow crystallized material was found to be blocking the inside of the braided second stage regulator hose. Although the hose had been in use for a few years, it showed no external abnormalities or any visible signs of deterioration.

In the process of trying to solve the mystery, it turned out that this was not an isolated case: A very same situation occurred on 22 July 2015 and was reported subsequently in a Technical Diving Blog(2). Although, again, no one was injured, the discovery has now prompted a wider, global investigation, which is still ongoing.

Above: 'Polymorphic crystallisation' inside nylon-braided hoses and inside a regulator. Regulator picture courtesy of Cozumel SCUBA Repair. Pictures published with permission of the photographers.

An analysis of the 'culprit' revealed it to be a form of 'polymorphic crystallisation' - a phenomenon associated with cyclical heating and cooling at oil-water interfaces(3). In both these cases, the crystallization seemed to be related to the molecular structure of the internal tube. The present theory is as follows: repeated cyclical heating and cooling of the internal

lining promotes this form of crystallisation in materials either unsuitable for this application, or affected by certain chemicals or bacteria. The sun heats the hose, whereas the flow of expanding breathing gas cools the internal surface of the hose down again. This process recurs with each dive, and the crystals grow and accumulate over time. Eventually, enough crystals form to encroach on the flow of gas, or they migrate towards the second stage regulator, resulting in significant failure of the breathing device.

The challenge now is how best to respond to the discovery:

- What do divers need to know right now; and
- What appropriate precautionary maintenance guidelines and early detection strategies should be implemented at this stage?

Previously, the standard safety recommendation regarding regulator hoses was that they should be inspected regularly for early signs of *external deterioration*. Perishing or abrasion of the outer rubber coating eventually predisposes hoses to rupture during pressurisation and even when in use. Rubber hoses are quite prone to this, which is why polymer-braided hoses were developed in the first place.

And here-in lies the problem: In the case of braided hoses, the outside still appears to be quite normal, flexible, with no obvious surface abnormalities. It is the *internal surface* that *deteriorates* -- completely invisible to a cursory external inspection!

However, it would be foolish to assume that this deterioration is limited to external 'braided' hoses. In the past, our hoses comprised a rubber inner hose, then a single braid layer for reinforcement, and finally a rubber, outer 'sealing' layer. In the modern era, the rubber inner hose is sometimes replaced with typically polyurethane or nylon hose (referred to as thermoplastic). The middle or reinforcing layer is a polymer filament braid, and the outer layer either a second braid – which as the advantage of telling you when inner hose has a leak, or a polyurethane or a synthetic rubber outer sealing layer.

The reality is that the newer, second stage hose with a thermoplastic inner layer may be vulnerable to degradation. In our industry, 'newer' means possibly even up to 15 years or longer. This does not, however, apply to synthetic rubber internal layers, which appear to be impervious to this phenomenon.

So, what should we recommend?

While DAN has been in contact with manufacturers of 'outer' braided hoses to assess possible causes as well as precautionary measures, we have a responsibility to inform divers about this much broader, critical safety concern. We feel it is important to advise divers as follows:

- All regulator hoses, including 'braided' hoses, have a limited service-life – irrespective of the external appearance, or the reinforcement and protection provided by hose protectors or the braiding itself.
- Unlike the rubber hoses of old, the internal section of all newer hoses which use a thermoplastic inner layer appears to be uniquely prone to 'polymorphic crystallisation', especially in hot, tropical locations. The phenomenon appears to be a gradual process, but the disruption of gas-flow and regulator function is unpredictable and invisible to external inspection.

- If there is any sign of gas-flow restriction in the regulator assembly, particularly when using a newer hose, the diver should stop using the regulator immediately. A careful inspection of the regulator and the hose should be performed. If the regulator is not the cause, suspect the hose.
- A physical examination including squeezing the hose every couple of inches to assess whether the hoses exhibits the same degree of flex should indicate if all is well. Any indication of a change in the resistance while squeezing along the length of the hose would be good sign that all is not well.
- This test, on the braided hose, is in fact much easier to perform than with the harder, outer 'rubberized' hoses.
- Do not clean out the inside of any hose with a detergent. Use warm water and a mild soap, and dry in a ventilated room.
- Definitely avoid any contact with salt water – bacteria in certain parts of the world have been known to lead to premature deterioration of the hose liner.
- Following this advice, and especially where regular inspections are performed on your hoses, will give you greater confidence that your hoses always perform as they should.

In closing, we ask you to please share this information with other divers and promote diving safety by promoting the following ABC strategy:

AIR AWARENESS: Make all divers aware of this problem and the need for regular equipment servicing.

BUDDY BREATHING: Practice emergency alternative gas source sharing procedures to ensure preparedness and appropriate action in the event of *regulator failure,* as well as out-of-gas situations.

CUSTOMER CHOICE: Be aware of what you buy - ensure that any hose purchased clearly shows information on the manufacturer, the production date and the standard used on the ends, and check that this information is consistent with the packaging.

We invite all divers who experience this inner-hose degradation to please contact DAN, preferably with pictures showing the condition of the inner hose. This will enable us to capture as much real information as possible, so that we can learn more about this phenomenon. Any new findings, cautions or advice will be shared with the diving community.

1. Vann R, Lang M. Recreational diving fatalities. *Undersea Hyperb Med* 2011; **38**(4): 257-60.
2. Davis A. Nylon-braided regulator hose diving emergency. 2015. http://scubatechphilippines.com/scuba_blog/regulator-hose-diving-emergency/#Polymorphic_Crystallization.
3. Douaire M, di Bari V, Norton JE, Sullo A, Lillford P, Norton IT. Fat crystallisation at oil-water interfaces. *Adv Colloid Interface Sci* 2014; **203**: 1-10

http://www.alertdiver.com/crystallized_hoses

ALERTDIVER

Invisible Crystals

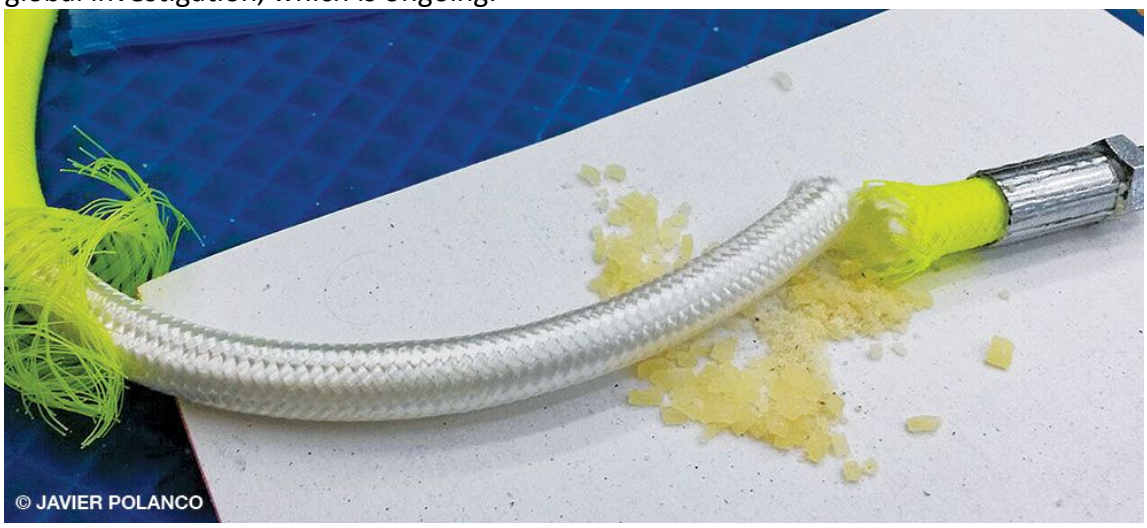
By Francois Burman, Pr. Eng, MSc
Crystallized nylon-hose interiors can cause regulator failures

Polymorphic crystallization inside hoses has recently emerged as a hazard divers should be aware of.

Scuba equipment failure or malfunction is a relatively rare factor in diving-related accidents and fatalities. When it does occur, the most common and hazardous malfunctions involve regulators and buoyancy compensator (BC) power inflators.[1] Thus, a recent report to DAN® of a regulator failure was not necessarily surprising, but the cause in this particular case turned out to be quite unusual.

Although the diver involved in the incident managed the situation very well, and no one was harmed, an inexperienced or nervous diver might not have been so fortunate. It was particularly strange that although the diver's cylinder was not empty, the gas flow had slowed and then ceased in a way that resembled an out-of-air situation. Closer examination of the equipment led to a puzzling discovery: A large amount of yellow crystallized material was blocking the inside of the braided second-stage regulator hose. The hose had been in use for a few years but showed no external abnormalities or signs of deterioration.

While trying to solve the mystery, we discovered this was not an isolated case. The same situation occurred July 22, 2015, and was reported subsequently in a technical diving blog.[2] Further reports from a hose manufacturer and at least one equipment-servicing workshop in a popular diving region revealed that these were not isolated events. Although no injuries have been reported, the discovery prompted a wider, global investigation, which is ongoing.



Degradation is a slow process, invisible until there is a total failure.

Analysis revealed the culprit to be a form of polymorphic crystallization — a phenomenon associated with cyclical heating and cooling at oil-water interfaces.[3] In both incidents, the crystallization seemed to be related to the molecular structure of the internal tube. The current theory is that repeated cyclical heating and cooling of the hose lining promotes this form of crystallization in materials either unsuitable for this application or affected by certain chemicals or bacteria. The sun heats the hose, then the flow of breathing gas cools down the internal surface of the hose again. This process recurs with each dive, and the crystals grow and accumulate over time. Enough crystals eventually form to encroach on the gas flow, or they migrate toward the second-stage regulator, resulting in significant failure of the breathing device.

So far the reported incidents have been in tropical climates with gear that is several years old. We have not received reports of this problem with vinyl hoses, and given the number of braided hoses out there (both as original components and replacement parts) the incidence is likely quite small. But because this hazard threatens divers' air supplies, it is of great potential interest to the dive community. The challenge is determining how best to respond to this discovery. It's important to identify what

divers need to know right now as well as what precautionary maintenance guidelines and early detection strategies they should implement at this stage.

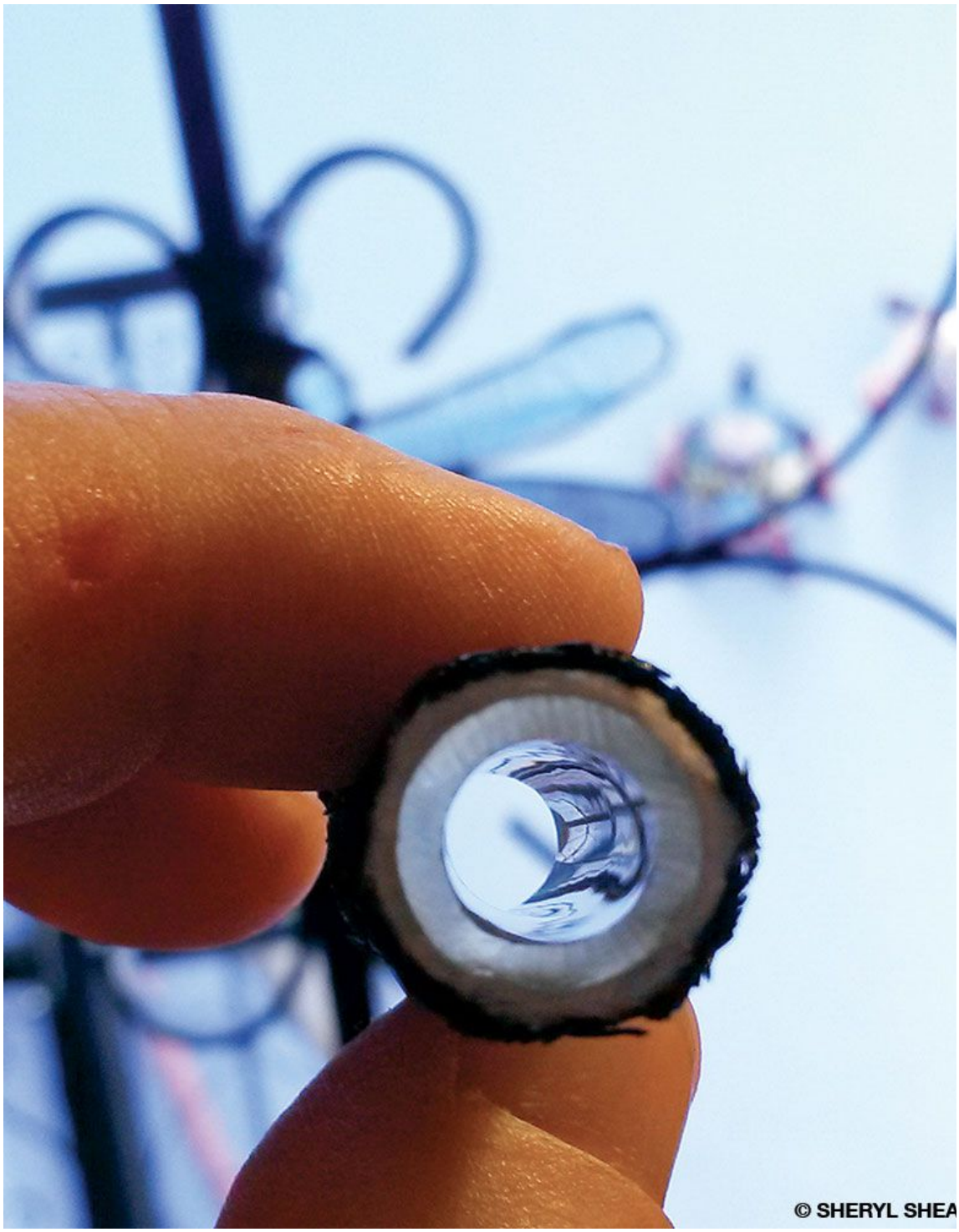
The standard safety recommendation regarding regulator hoses has been that they should be inspected regularly for signs of external deterioration. Disintegration or abrasion of the outer rubber coating eventually predisposes hoses to rupture during pressurization or even when in use. Rubber hoses are quite prone to this condition, which is why polymer-braided hoses were developed. But herein lies the problem: The outside of braided hoses can appear normal, flexible and free from obvious abnormalities, while a deteriorated internal surface would be completely invisible to a cursory external inspection.

This open hose shows the extent of degradation.

It would be premature to speculate that this deterioration is limited to braided hoses. Previously, hoses comprised a rubber inner hose, a single braid layer for reinforcement and finally a rubber outer sealing layer. Today the rubber inner hose is sometimes replaced with a polyurethane or nylon hose (referred to as thermoplastic). The middle or reinforcing layer is a polymer-filament braid, and the outer layer is either a second braid — which has the advantage of indicating when the inner hose has a leak — or a polyurethane or synthetic-rubber sealing layer.

Newer second-stage hoses with a thermoplastic inner layer may be vulnerable to degradation. This risk does not apply to internal layers of synthetic rubber, which appear to be impervious to this phenomenon. DAN Research would normally wish to conduct more in-depth analysis with a wider sample of defective hoses, but because this is a potential hazard to regulator function we prefer to err on the side of caution and report this phenomenon now.

What Does DAN Recommend?



This hose interior is not affected by polymorphic crystallization.

DAN has contacted manufacturers of outer braided hoses to assess possible causes and precautionary measures, and we feel it is important to advise divers as follows:

- All regulator hoses, including braided hoses, have a limited service life regardless of external appearance or reinforcement and protection provided by hose protectors or the braiding itself. The failed hoses we have seen are more than five years old.
- The internal section of newer hoses with a thermoplastic inner layer appears to be uniquely prone to polymorphic crystallization, especially in hot, tropical

locations. The phenomenon appears to be a gradual process, but the disruption of gas flow and regulator function is unpredictable and invisible to external inspection.

- If there is any indication of gas-flow restriction, particularly when using a newer hose, the diver should immediately stop using the regulator. Perform a careful inspection of the regulator and the hose. If the regulator is not the cause, suspect the hose.
- Physically examine hoses by squeezing them every inch or so to assess whether they exhibit the same degree of flexibility. Any change in resistance while squeezing along the length of the hose would be a sign of a possible problem. This test is much easier to perform with braided hoses than with harder, outer rubberized hoses.

Replace old hoses, limit hoses' exposure to high temperatures, and follow manufacturers' maintenance recommendations.

Following this advice, especially the recommendation to regularly inspect hoses, will give you greater confidence that your hoses will perform as they should. Advocate for dive safety by promoting the following ABC strategy:

- **Air awareness:** Make all divers aware of this problem and the need for regular equipment servicing.
- **Buddy breathing:** Practice emergency air-sharing procedures to ensure preparedness for and appropriate action in the event of regulator failures or out-of-gas situations.

- **Customer choice:** Ensure that any hose purchased displays on the ends information about the manufacturer, the production date and the standard used. Check that this information is consistent with that on the packaging.

We ask all divers who observe this inner-hose degradation to please email DAN at research@dan.org, preferably providing pictures that show the condition of the hose. This will enable us to capture as much information as possible so we can learn more about this phenomenon. We will share any new findings, cautions and advice with the diving community.

References

1. Vann R, Lang M. Recreational diving fatalities. Undersea Hyperb Med 2011; 38(4): 257-60.
2. Davis A. Nylon-braided regulator hose diving emergency. Scuba Tech Philippines. July 22, 2015. scubatechphilippines.com/scuba_blog/regulator-hose-diving-emergency/#Polymorphic_Crystallization. Accessed December 7, 2016.
3. Douaire M, di Bari V, Norton JE, Sullo A, Lillford P, Norton IT. Fat crystallisation at oil-water interfaces. Adv Colloid Interface Sci 2014; 203: 1-10.